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Transition Metal Rimmed Calixarenes And Their Supramolecular Chemistry

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TRANSITION METAL RIMMED CALIXARENES

AND

THEIR SUPRAMOLECULAR CHEMISTRY

BY

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ABSTRACT

This thesis describes the design and the synthesis of novel anion and cation receptors in which sets of transition metal atoms are introduced on the rims of calixarene bowls.

A bowl-shaped calixresorcinarene 1 has been derivatized to incorporate either four phosphonite units to give a phosphonito-cavitand 2 or eight phosphinite units to give a phosphinito-calixresorcinarene 3. These derivatives have been used as multidentate ligands to incorporate transition metals on the upper-rim of the calixresorcinarene bowl. The chlorogold(I) complex of 4, $2(AuCl)_4$ which was characterized by an X-ray structure determination, is shown to contain three AuCl units around the upper rim of the bowl with the fourth AuCl unit folded inside the cavity.

The tetradentate phosphonito-cavitand, 2 has also been used in the synthesis of several tetracopper(I) and tetrasilver(I) complexes. The tetracopper(I) complex 5 and tetrasilver(I) complex, 6 have been shown to act as size-selective hosts for halide inclusion. Iodide is preferred over chloride as guest since it is large enough to coordinate to all four copper atoms in a unique μ_4-face-bridging bonding mode. This $Cu_4(\mu_4\text{-}I)$ and a similar $Ag_4(\mu_4\text{-}Cl)$ bonding mode have been characterized by X-ray structure determinations on suitable anionic complexes. The anion inclusions found for the transition metal rimmed bowl complexes are unique in supramolecular chemistry.

Both the copper and silver complexes, **5** and **6** proved to be powerful and versatile metal cation receptors. The cation inclusions of **5** and **6** are driven by chelating effects of four chloride donors and enhanced by the occluded anion. X-ray analysis on $\underline{5}^{-}.Cs^{+}$ indicated that the two included Cs^{+} ions were sandwiched by two anions of **5**. Similarly, one Hg^{2+} ion in $\underline{6}^{-}_{2}Hg^{2+}$ were also sandwiched by two anions of **6**, but the Hg^{2+} appeared to be coordinated with the chloride ligands and almost buried inside the cup defined by the four chloride ligands on the rim and the occluded chloride ligand.

Tetra-O-alkyl-calix[4]arenes are shown to act as hosts for the Ag^{+} ion. The structure of one silver(I) complex has been determined by an X-ray structure analysis. The silver ion is held in the cavity of the calixarene and is weakly coordinated to two arene groups and one methoxy group.

This thesis is dedicated to..

My Dear Father

and

Mother...

獻給我

親愛的父親和母親

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KEY ABBREVIATIONS

Å	=	Angstrom
Anal. Calc.	=	Analysis calculated
Bu^t	=	Tertiary Butyl
br	=	Broad
c	=	cis
COD	=	1,5-Cyclooctadiene
Cp	=	Cyclopentadienyl
d	=	Doublet
dppm	=	Bis(diphenylphosphino)methane
e	=	Electron
EDX	=	Energy dispersive X-ray
Et	=	Ethyl
F_o	=	Observed Structure Factor
F_c	=	Calculated Structure Factor
FAB	=	Fast Atom Bombardment
HOMO	=	Highest Occupied Molecular Orbital
IR	=	Infrared
J	=	Coupling Constant
LUMO	=	Lowest Unoccupied Molecular Orbital
M	=	Metal Center
Me	=	Methyl
MHz	=	Megahertz
MO	=	Molecular Orbital
M.p.	=	Melting Point
MS	=	Mass Spectrum
nm	=	Nanometer
NMR	=	Nuclear Magnetic Resonance
Ph	=	Phenyl
R	=	Alkyl or Aryl
s	=	Singlet for NMR; strong for IR
t	=	Triplet for NMR; trans for conformation
THF	=	Tetrahydrofuran
UV	=	Ultraviolet
X	=	Halogen
Z	=	Number of Molecules Per Unit Cell
λ	=	Wavelength
ν	=	Frequency
δ	=	Chemical Shift
σ	=	Standard Deviation

Chapter One

INTRODUCTION TO

THE SUPRAMOLECULAR CHEMISTRY OF CALIXARENES

1.1 INTRODUCTION

Supramolecular chemistry is a branch of chemistry studying molecular interactions or intermolecular bonds. It is a highly interdisciplinary field covering chemical, physical and biological features of chemical species which are held together and organized by means of intermolecular interactions. In supramolecular chemistry, macrocyclic compounds are the most extensively studied systems.

Macrocyclic compounds are polydentate ligands containing their donor atoms attached to a cyclic backbone. The fact that macrocyclic complexes are involved in a number of fundamental biological systems has long been recognized.[1-3] The possibility of using synthetic macrocycles as models for biological systems, such as photosynthesis in plants and oxygen transport in mammals, has provided an impetus for such research. Apart from the biological implications, the chemistry of macrocyclic ligands is closely related to a diverse number of other areas, such as metal ion catalysis, organic synthesis, metal-ion discrimination, and analytical methods as well as a number of potential industrial and medical applications. All these attractive areas have contributed in making macrocyclic chemistry become one of the most popular areas in chemistry.[4,5]

Calixarenes are macrocyclic ligands composed of phenolic rings bridged by methylene groups. The chemistry of the calixarenes is abundantly described in several current books and review articles.[6-14] The origins of calixarenes, however, can be traced back to von Böyer's discovery of phenol-formaldehyde resins in the 1870s.[15] Their potential as molecular receptors or enzyme mimics was first noted by Gutsche in 1978.[6] Subsequently, calixarene chemistry has developed very fast and has become particularly significant in the supramolecular chemistry during the past sixteen years.[5]

One of the principal reasons for investigation of calixarenes in recent years is that they have the ability to act as a bowl to hold guests.[8] The calixarenes share the symmetric beauty with the other important supramolecules such as crown ethers, cyclodextrins and cryptands. In contrast to the simple crown ethers, the calixarenes are bowls rather than loops. In contrast to the cyclodextrins and most cryptands, the calixarenes are accessible by simple laboratory synthesis. In contrast to the crown ethers, the cyclodextrins and the cryptands, calixarenes appear to be a relatively new member in the macrocyclic family.[6] Several other advantages of the calixarenes, such as good chemical and thermal stability, possible functionalization and the fact that they are relatively cheap compared with crown-ethers, cyclodextrins and cryptands, have attracted more chemists into the area.[14]

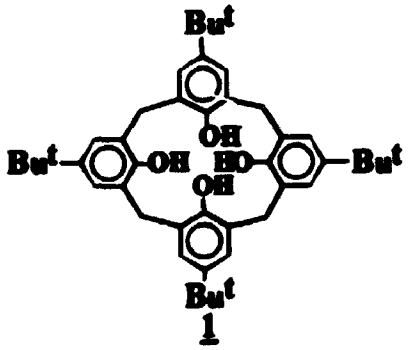
1.2 NOMENCLATURE OF CALIXARENES

The name 'calixarene' was originally generated from the bowl-shaped phenol-derived cyclic tetramer in the conformation in which all four aryl groups are oriented in the same

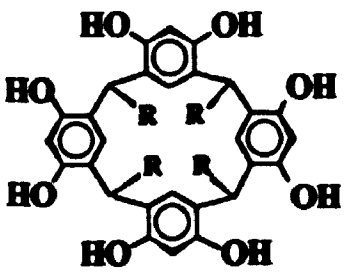
direction. (Gk. calix, a chalice or a cup; arene, aromatic ring). To define the number of phenyl rings in a calixarene, a bracketed number is inserted between calix and arene as calix[n]arene. To indicate which phenol that the calixarene is derived from, a prefix was added before its name or inserted in its middle. For example, the calix[4]arene derived from *p-tert*-butylphenol is called *p-tert*-butylcalix[4]arene and the calixarene derived from resorcinol is called calix[4]resorcinarene.

1.3 PREPARATION OF CALIXARENES

One of the reasons that calixarenes enjoy so much attention is that they can be prepared easily from simple starting materials in large quantities. Since the beginning of phenol-formaldehyde chemistry over a century ago,[15] several ways to prepare calixarenes have been developed.[16-19] The stepwise synthetic routes which give various calixarene derivatives with different substituents had been introduced by Hayes and Hunter.[6,9,20] However, the preparations of both *p-tert*-butylcalix[4]arene **1**, and calix[4]resorcinarene **2**, remained a tedious event till recently.[21-24]



1



2 R = Me, Et, ...,... CH_2CH_2Ph

1.3.1 One Step, Base-induced Synthesis of Phenol-derived Calixarenes

In 1989, the Gutsche group developed a reliable, reproducible procedure to prepare *p-tert*-butylcalix[4]arene 1 in high yield (~80%) as illustrated in Figure 1.[21,22]

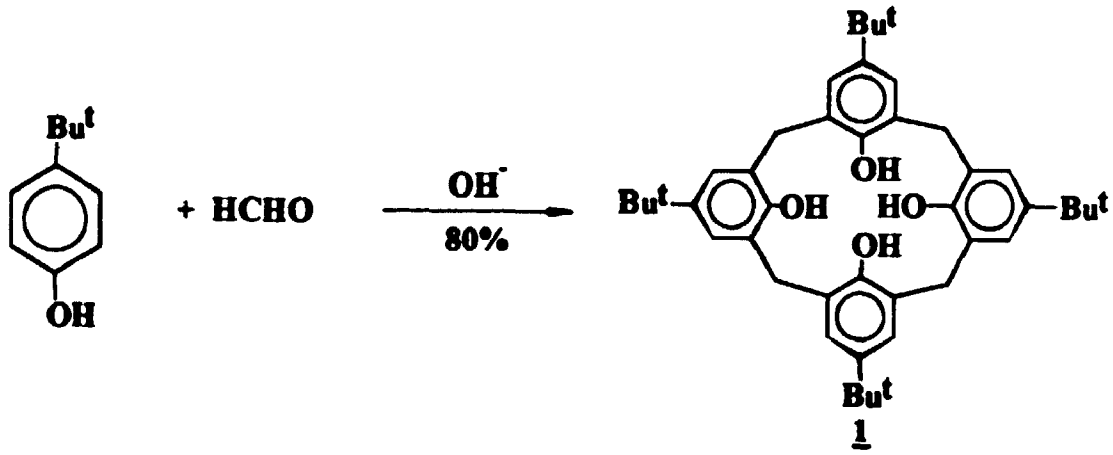


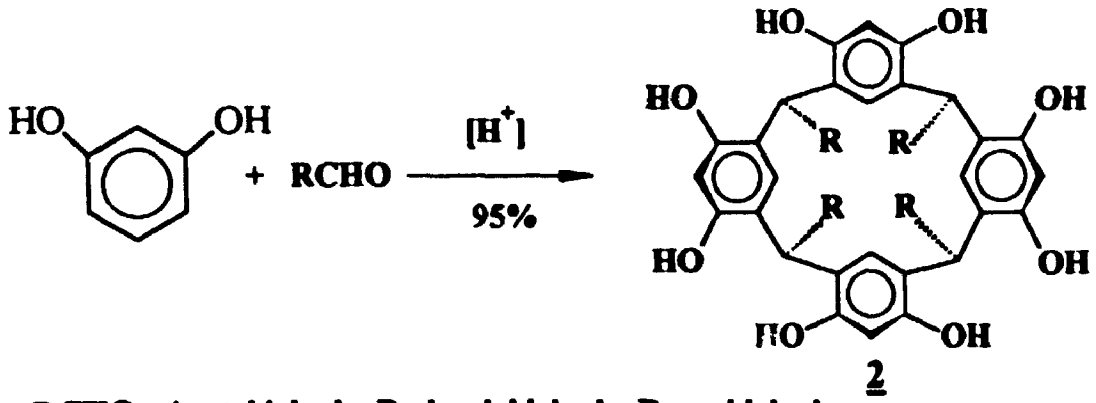
Figure 1. Preparation of phenol-derived calixarenes

By controlling the reaction conditions, the cyclic hexamer or octamer could also be obtained in 80% or 60% yield , respectively. The calix[n]arenes with an odd number of *t*-butylphenol units (n=5 or 7) have also been prepared by direct condensation but with much lower yields. The higher number (n = 9-16) have been isolated by chromatographic techniques.[7,9] The calixarenes bearing different substituents (R or Ar) in the *para* position also can be obtained by the one-pot procedures.[6]

1.3.2 One Step, Acid-catalyzed Synthesis of Resorcinol-derived Calixarenes

Cram and coworkers developed an acid catalyzed procedure for synthesis of calix[4]resorcinarenes[23] 2 in 95% yield on a large scale in 1989 as illustrated in Figure

2. In contrast to phenol-derived calix[4]arenes, larger cyclic oligomers of resorcinol-derived calixarenes have not yet been observed.



RCHO : Acetaldehyde, Dodecylaldehyde, Benzaldehyde, Thiophenecarboxaldehyde, Ferrocenecarboxaldehyde.....

Figure 2. Preparation of resorcinol-derived calix[4]arenes

1.4 STRUCTURES AND CONFORMATIONS OF CALIXARENES

One of the other appealing features of calixarenes is their three-dimensional structure. The molecular models showed that calixarenes can never be planar, but can be bowl-shaped, although numerous conformations are possible by rotating the phenolic moieties about the Ar-CH_2 bonds.

1.4.1 Structures

More than 50 years ago, cyclic structures had already been proposed for some of these

calixarenes.[25-28] However, the final definitive proof came from crystal structure studies by the Andreetti group in 1979.[29] X-ray crystallographic studies showed that the structure of a *p-tert*-butylcalix[4]arene was a cyclic tetramer in a bowl shape designated as the 'cone' conformation, as shown in Figure 3. Because of this conformation, the calixarenes possess intramolecular cavities whose dimensions are expected to increase as the number of aromatic units [n] increases. An especially interesting feature of the structure is that a toluene molecule was included in its cavity. Following that, many crystal structures of calixarene derivatives have been solved and give the ultimate proofs for the structures and conformations of calixarenes and their tremendous host properties.[30-37]

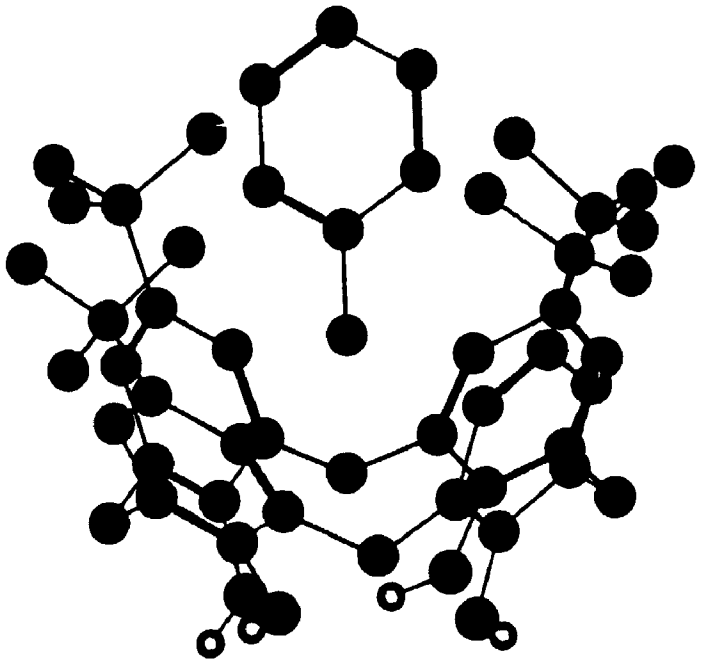


Figure 3. Structure model of endo complex of *p-tert*-butylcalix[4]arene with toluene

1.4.2 Conformations

Dating from the 1950s,[38] it has been realized that the phenol-derived calix[4]arenes can

exist in one of the four shapes, cone, partial cone, 1,2-alternate and 1,3-alternate forms, as shown in Figure 4. Each of these conformers has been proved by X-ray crystallography in the solid state. In solution, these conformers also can be distinguished unambiguously by ^{1}H or ^{13}C NMR techniques.[39-41]

With resorcinol-derived calixarenes, the same four conformational possibilities, cone, 1,3-alternate, flattened cone and flattened partial cone were observed. Due to the non-symmetrical bridging -CHR- groups, six different diastereomers are possible for the cone conformer (cccc, ccct, ctct, cctt, cttt, tttt) as pictured in Figure 5. Fortunately, in many cases, the all cis isomer (cccc) is the predominant compound after longer reaction times. The most interesting cccc isomer has a cone-like structure with four pairs of intramolecular hydrogen-bonded hydroxyl groups in axial positions.

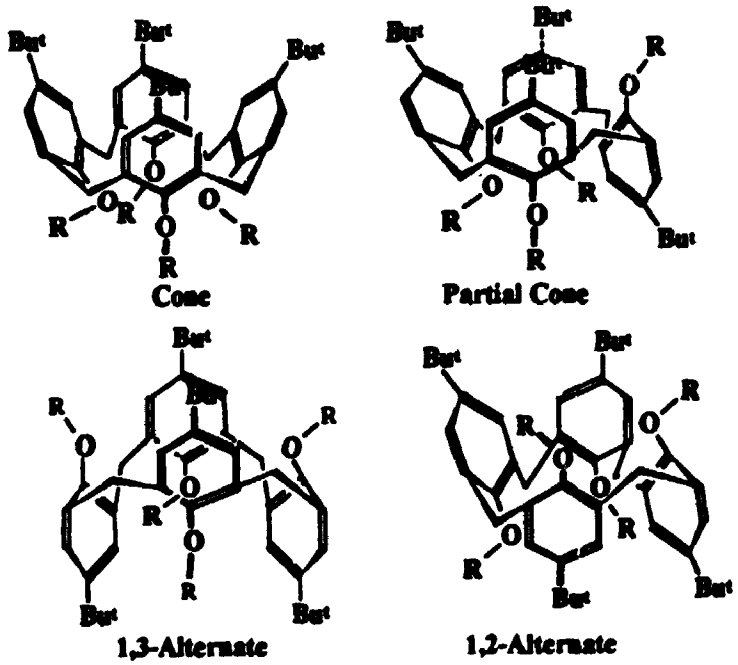


Figure 4. Four basic conformations of *p-tert*-butylcalix[4]arene ethers

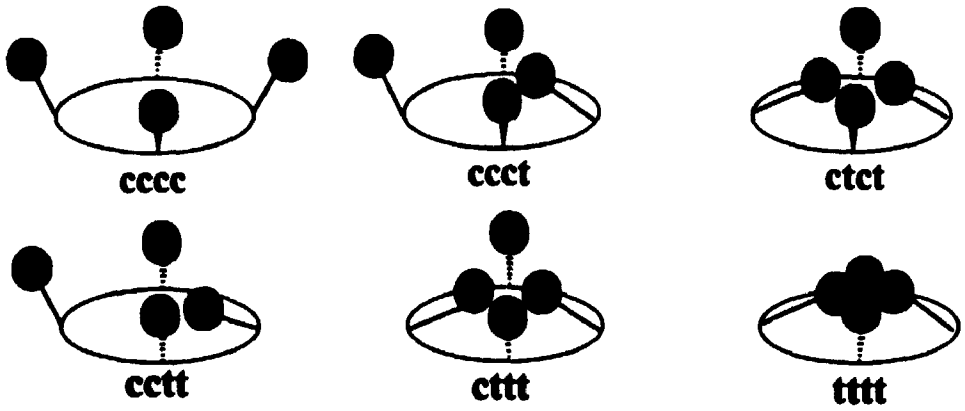


Figure 5. Six diastereoisomers of resorcinol-derived calix[4]arenes in cone conformation

1.4.3 Factors Which Affect the Conformations

Although, the calix[4]arenes can form cavities which are large enough to engulf ions or molecules, their conformational mobility makes them ephemeral rather than permanent bowls. All of the calixarenes are conformationally mobile in solution especially when they lose the hydrogen bonding effects as the OH groups are replaced by OR groups. The degree of mobility varies from one ring system to another. All four of the conformations for a calix[4]arene are accessible by rotations of the aryl ring unit through the annulus. The rotation is rather fast on the laboratory time scale. By employing temperature-dependent ^{1}H NMR measurements (the coalescence temperature in a 100MHz spectrum is 47°C)[35], the rate of interconversion can be calculated to be ca. 150s^{-1} with an energy barrier of $\Delta G^{\neq}$=65.7kJ/mol. However the rate of interconversion is largely influenced by the temperature, the polarity of the solvent, the substituents on the aryl rings and metal cation complexation. For example, it is possible to freeze out the conformational mobility by lowering the temperature or by introducing bulky R groups on the lower rim

of phenol-derived calixarenes. Details of these factors have been well explained in the literature.[6-9]

1.5 FUNCTIONALIZATION OF CALIXARENES

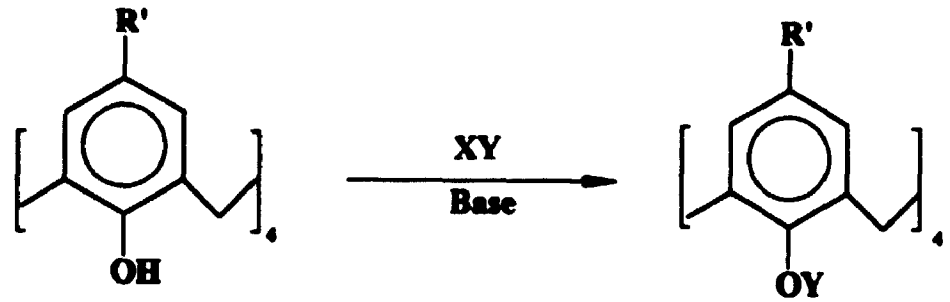
Many of the interesting properties of calixarenes such as complexation and catalysis depend upon the presence of appropriate functional groups. In terms of functionalization the calixarenes are much more versatile than crown ethers and cryptands. Various methods for introducing different functional groups to the calixarene bowl have been developed. These features, in combination with their interesting conformational properties, make the calixarenes highly fascinating and inspiring for many chemists.

1.5.1 Esterification and Etherification

Since the lower rim of phenol-derived calixarenes and the upper rim of resorcinol-derived calixarenes are already functionalized with OH groups, the most obvious way to functionalize the calixarenes is to replace the abundant OH groups with OR groups as Figure 6 shows.

This approach has been exploited by several groups.[42-49] In the presence of excess acylating, aroylating or alkylating reagents, the completely substituted esters or ethers are frequently obtained. These esters and ethers can apparently exist in any one of the four conformations: cone, partial cone, 1,2-alternate or 1,3-alternate depending upon the

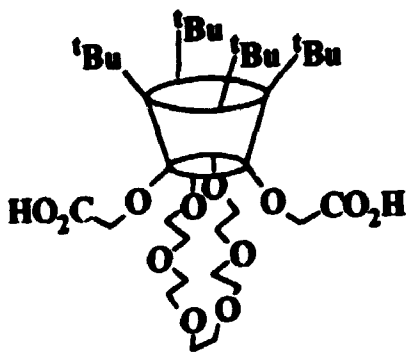
reaction conditions and the reagents used.[8] In this way, the conformations of calixarenes can be adjusted. Some significant selective cation binding properties would result from appropriate esterification and etherification by introducing functional groups, such as ester, ketone, amide, thioamide and carboxylic acid derivatives.[50,51]



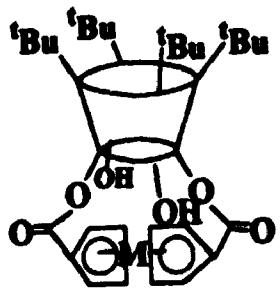
R' = Bu^t, H; Y = R, RCO, ArCO, CH_2CO_2R, CH_2CONHR, CH_2CO_2H
Allyl, $SiMe_3$, TsO

Figure 6. Functionalization of calixarenes *via* esterification and etherification

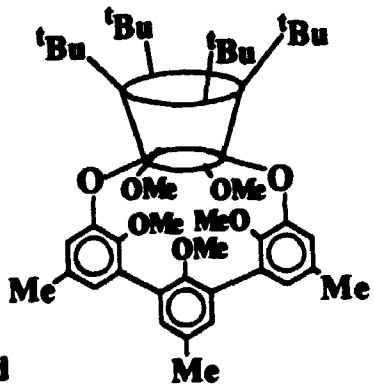
The etherification and the esterification do not always result in complete substitution. 1,3-substituted products are often formed.[52] Advantage has been taken of partial substitution reactions in the preparation of bridged compounds, such as calixcrown 3,[30] metallocene-bridged calixarene 4,[53] and calixspherand 5[54]



Calixcrown 3



Metallocene-bridged Calixarene 4



Calixspherand 5

The monosubstituted calix[4]arene derivatives have been obtained in the cone conformation, as indicated by ^{1}H NMR spectra although no X-ray structure has been reported yet.[55,56] After the methylation of three OH groups, the calix[4]arene still maintains the cone conformation, but it appears more distorted than that observed in the dimethyl derivative.[57,58]

1.5.2 Electrophilic Substitution

The introduction of *p*-functional groups in calixarenes requires the replacement of the *p*-alkyl moieties. Fortunately, the para-substituent of calixarenes can be easily removed by a reverse Friedel-Crafts reaction with aluminium chloride in toluene in good yield.[47,48] Nearly all types of aromatic electrophilic substitution such as alkylation,[55,59] acylation,[60] bromination[61] nitration[62] and sulphonation[63] are becoming possible, leading to calixarenes with various substituents or functional groups in para positions as illustrated in Figure 7. These types of reactions have been particularly effectively used by Shinkai for the preparation of water soluble *p*-sulphonato calixarenes.[64-66]

The synthesis of *p*-phenylcalixarene is especially noteworthy due to its rigid and extended hydrophobic cavity. Several methods to introduce phenyl groups to the para position of calixarenes have been reported. Arduini and coworkers[67] used a *p*-iodocalix[4]arene intermediate to prepare *p*-phenylcalixarenes whereas Atwood and coworkers[68] treated *p*-bromocalix[4]arene tetramethyl ether with arylboronic acid in the presence of $Pd(PPh_3)_4$ as catalyst to obtained *p*-phenylcalixarene in 75% yield as illustrated in Figure 8.

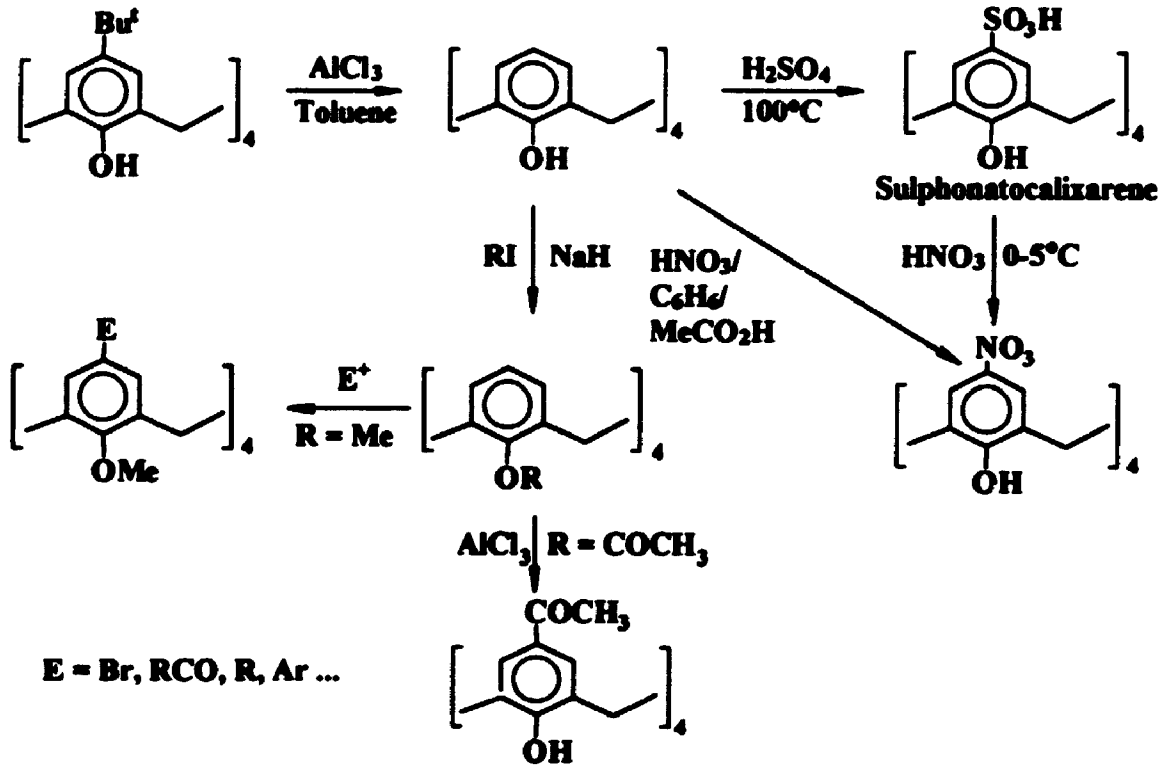


Figure 7. *p*-Functionalization of calixarenes *via* electrophilic substitution routes

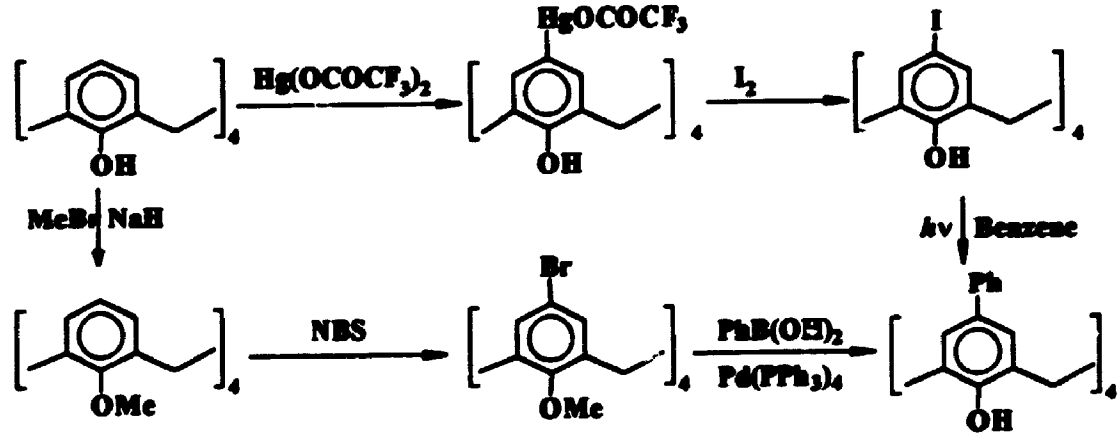


Figure 8. Preparation of *p*-phenylcalixarenes

1.5.3 Claisen Rearrangement

One of the most productive functionalization methods yet employed is the *para*-Claisen rearrangement.[53,54] Heating the allyl ethers of the calixarenes affords reasonably good yields of *p*-allylcalixarenes which in turn can be converted to a variety of *p*-functionalized calixarenes as illustrated in Figure 9.

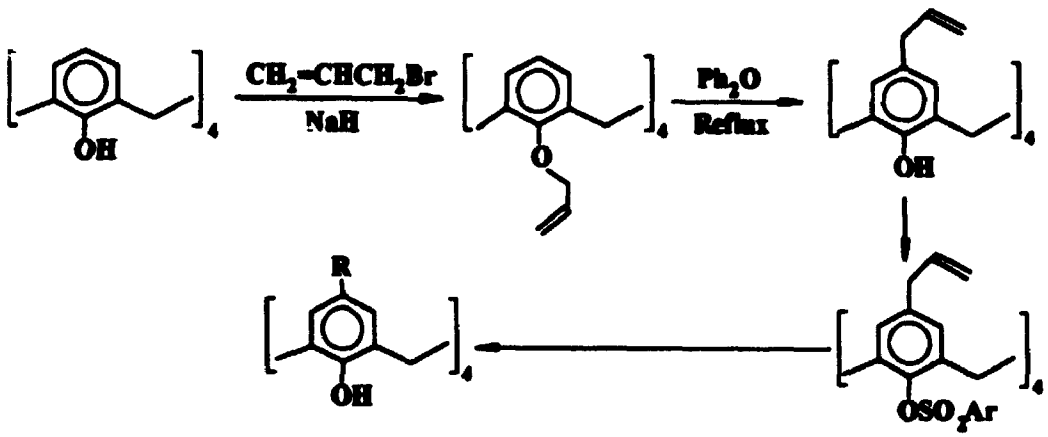


Figure 9. *p*-Functionalization of calixarenes *via* the *p*-Claisen rearrangement route

1.5.4 *p*-Quinonemethide Route

Taking advantage of the nucleophilic character of the *para*-position of phenolates, calix[4]arene can react with formaldehyde in the presence of the secondary amines to give Mannich-type products.[69,70] These compounds can be converted into the corresponding quaternary ammonium derivatives, which can further react with two equivalents of nucleophile to afford functionalized products *via* a *p*-quinonemethide intermediate as illustrated in Figure 10.[71]

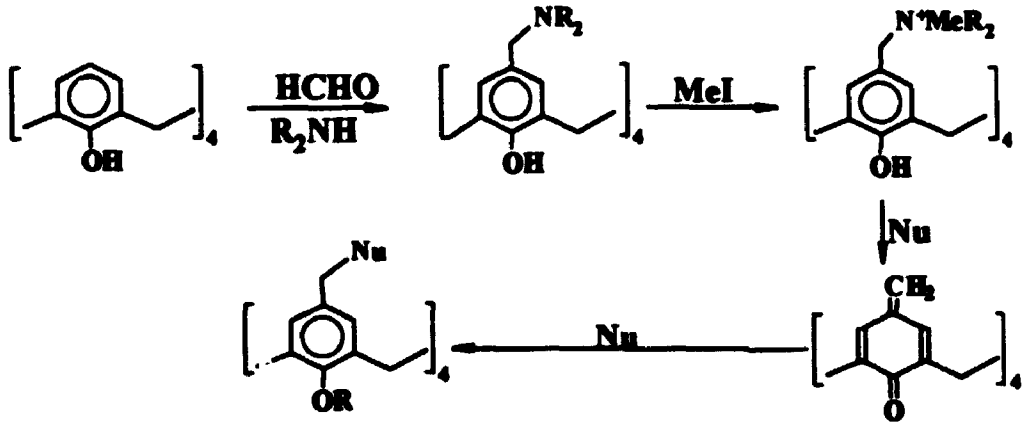


Figure 10. *p*-Functionalization of calixarenes *via* the *p*-quinonemethide route

1.5.5 *p*-Chloromethylation

Perceiving the convenience of introducing functional groups by way of the CH_2Cl group, two routes have been developed to give a calixarene with four CH_2Cl groups at the *para* positions as illustrated in Figure 11.[69-72] The chloromethylated calixarenes can be further functionalized by nucleophilic replacement of the halogens.[73]

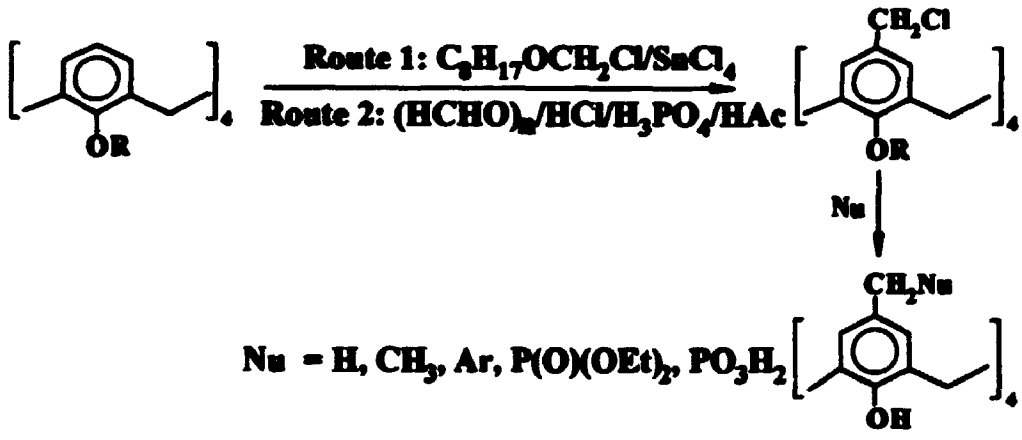


Figure 11. *p*-Functionalization of calixarenes *via* the *p*-chloromethylation route

1.5.6 Dehydroxylation and Substitution of OH Groups with NH_2 and SH Groups

Recently, an approach to alter the lower rim by removing OH groups[74,75] or to replace OH groups with NH_2[76] and SH[77,78] groups has been reported. Diamino-*p-tert*-butylcalix[4]arene[76] can be obtained by treatment of the *p-tert*-butylcalix[4]arene bis(diethylphosphate) ester with KNH_2 at -78°C. Similarly a tetramercaptocalixarene[77,78] in the 1,2-alternate conformation was obtained by treatment of *p-tert*-butylcalix[4]arene with N,N-dimethylthiocarbamoyl chloride, followed by the Newman-Kwart rearrangement and reduction with $LiAlH_4$, as illustrated in Figure 12.

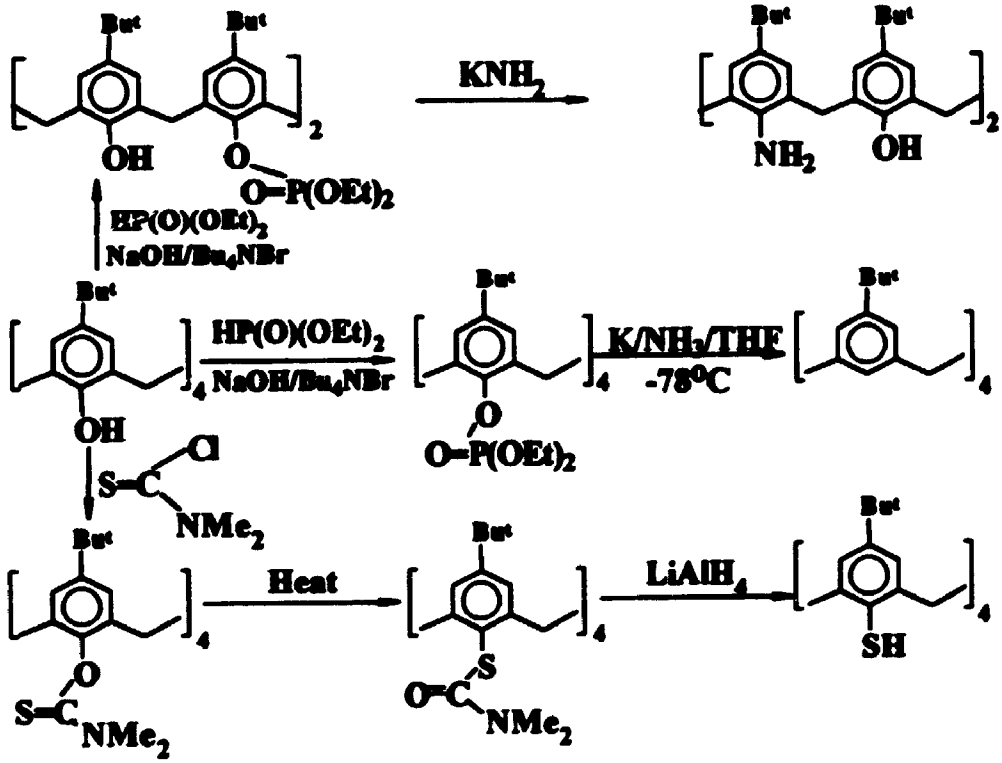


Figure 12. Dehydroxylation and substitution of OH groups by NH_2 and SH groups

1.5.7 Calixquinone Route

Further potentially important modifications of the calixarenes skeleton include the oxidation of phenolic units to *p*-quinone[79] which can subsequently undergo reduction to hydroquinone as illustrated in Figure 13.

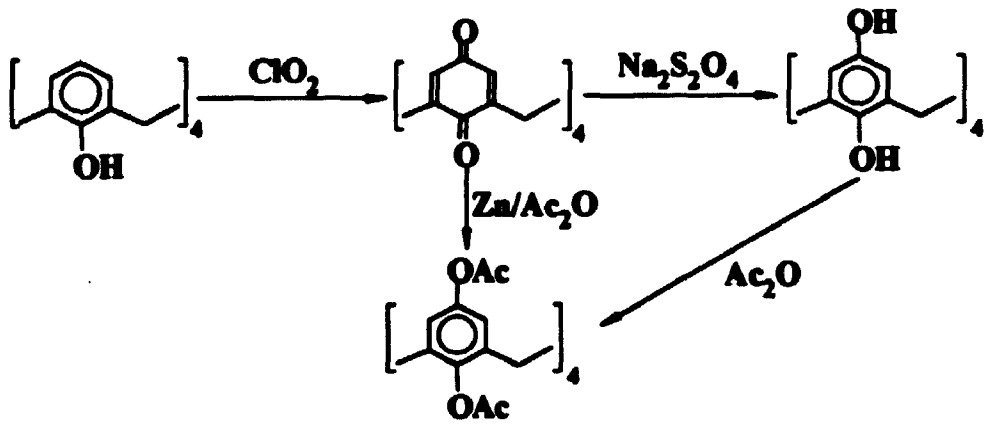
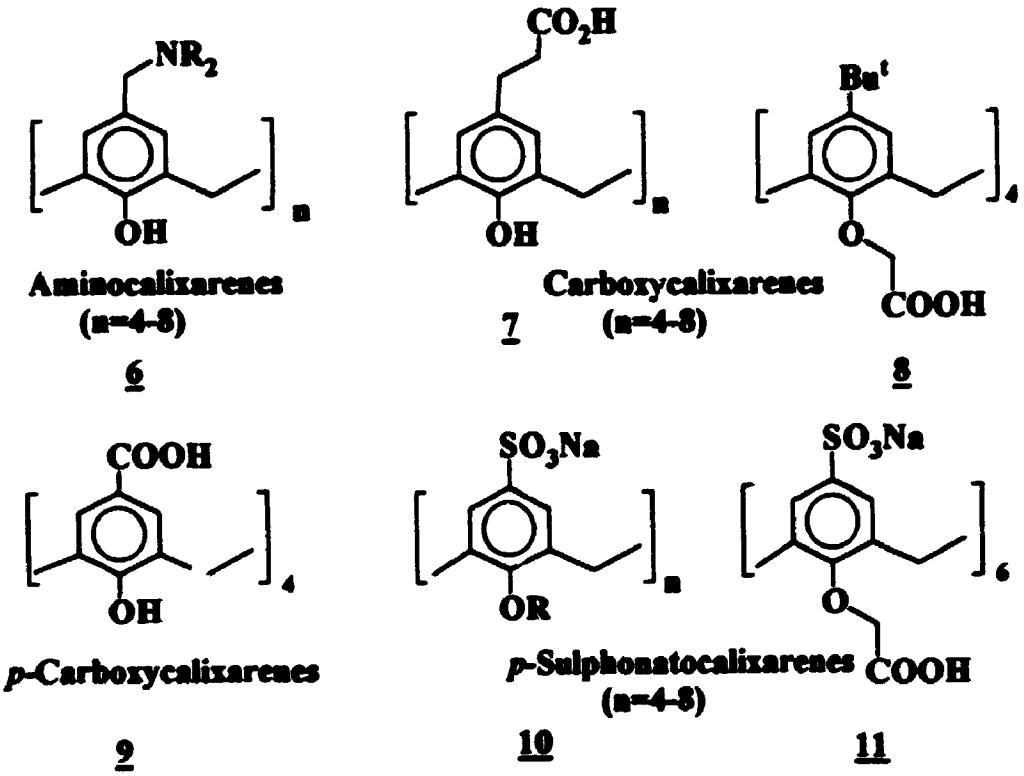


Figure 13. Functionalization of calixarenes *via* a calixquinone route



1.6 WATER SOLUBLE CALIXARENES

The special interest in the water soluble calixarenes, such as compounds 6-11, stems from their ability to interact with ions and molecules in aqueous solution and to perform catalysis.[80] The first water soluble calixarene, the tetracarboxymethyl calixarene ether 7, was obtained by Ungaro and his coworkers with solubilities of ca. 10^{-3}M.[42] Considerably more soluble calixarenes (~0.1M) are the sulphonated calixarenes 8 and 11 prepared by Shinkai.[63-66]

By using X-ray diffraction, Atwood has discovered a water included complex of *p*-sulphonatocalixarene.[81] The water molecule occupied the conical cavity with its two hydrogen atoms directed towards the two opposite benzene rings. The structure may provide clues about how water molecules interact with aromatic moieties in biological systems. Alkali metal salts of *p*-sulphonatocalix[4]arenes, such as Na_5[calix[4]arenesulphonate].$12H_2O$ and Na_5[calix[4]arenesulphonate].acetone.$8H_2O$, have been shown to exist in the solid state as structures in which the calixarene is in the cone conformation and the alkali metal ions along with water molecules form alternating layers that bear a close resemblance to clay minerals.[82,83] Some transition metal complexes of water-soluble calixarenes have been prepared and characterized. It is demonstrated by X-ray techniques that transition metal species, such as $Cr(OH_2)_6^{3+}$, $Yb(OH_2)_7^{3+}$ and $Cu(OH_2)_4^{2+}$ are intercalated within the hydrophillic layer by interacting with sulphonate oxygen atoms and an acetone molecule sits in the calixarene cavity.[84] Atwood also reported that the water soluble calixarenes can assemble to large aggregates

with transition metal complexes by second-sphere coordination.[86] An example of a two-component complex of *p*-sulphonatocalixarene and $[Cu(NC_5H_5)_2]^{2+}$ is illustrated in Figure 14 in which one pyridine ring of $[(H_2O)_4Cu(NC_5H_5)_2]^{2+}$ is imbedded in the calixarene cavity while the other is intercalated into the calixarene bilayer. The hydrophobic effect or van der Waals forces are believed to be responsible for the formation of the second-sphere coordination complexes or so called supramolecular assembly.

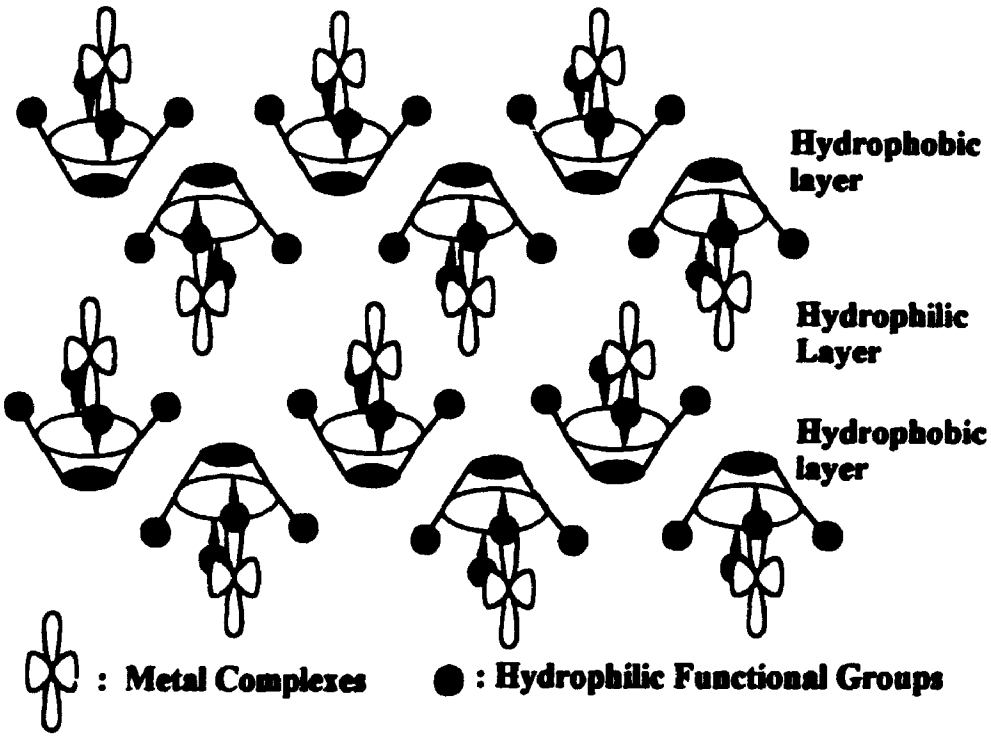


Figure 14. Molecular packing in supramolecular assemblies

1.7 CAVITANDS AND CARCERANDS

The treatment of an appropriate calixresorcinarene with excess of CH_2BrCl under basic conditions gave a corresponding product which was named a cavitand by Cram.[87-90] The

cavitands containing $(CH_2)_n$(n=2-3) or R_2Si bridges were also synthesized by treatment of the calixresorcinarene with correspondent X-A-Y reagent as Figure 15 shows.[87-92] Various functional groups have been put on the top of the aromatic rings of these calixresorcinarene frameworks, thus making it possible to construct molecular bowls with various shapes, sizes and functionalities.[93] These cavitands are bowl-shaped molecules with deeper cavities than the precursors. The depths of their cavities vary with X and R. The complexation behaviour of the cavitands has been studied in great detail by Cram and coworkers. Most of these cavitands crystallized as solvates. The crystal structures of inclusion complexes with chloroform, DMF, benzonitrile, fluorobenzene, carbon disulphide, propyne, CH_2Cl_2, acetone, acetonitrile, water, benzene, toluene, cyclohexane and dioxane and even argon and Cs^+ have been reported.[2,94-100] Although these guests could not be removed at high temperature and low pressure, they were replaced easily by solvents such as $CDCl_3$.[87] For example, the complex with $CHCl_3$ is stable enough to resist decomposition at 100°C and 10^{-5} mm Hg, but no obvious chemical shift differences of endo-$CHCl_3$ and free $CHCl_3$ could be observed by ^1H NMR techniques, nevertheless, the X-ray structures of these complexes clearly showed the endo-calix inclusions.[87]

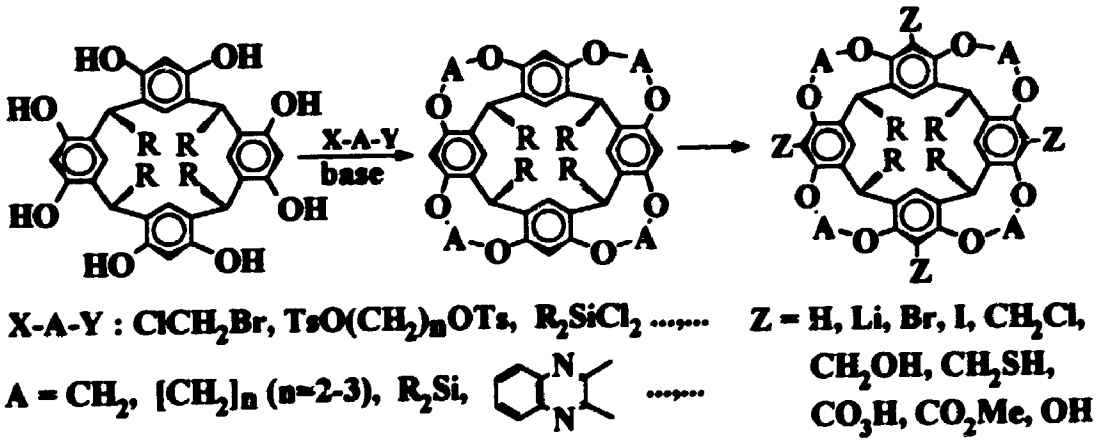


Figure 15. Preparation and functionalization of cavitands

The most unusual of all of the host-guest complexes that have been synthesized so far are those involving carcerands, whose structures consist of a pair of cavitands joined upper rim to upper rim in a football shape as illustrated in Figure 16.

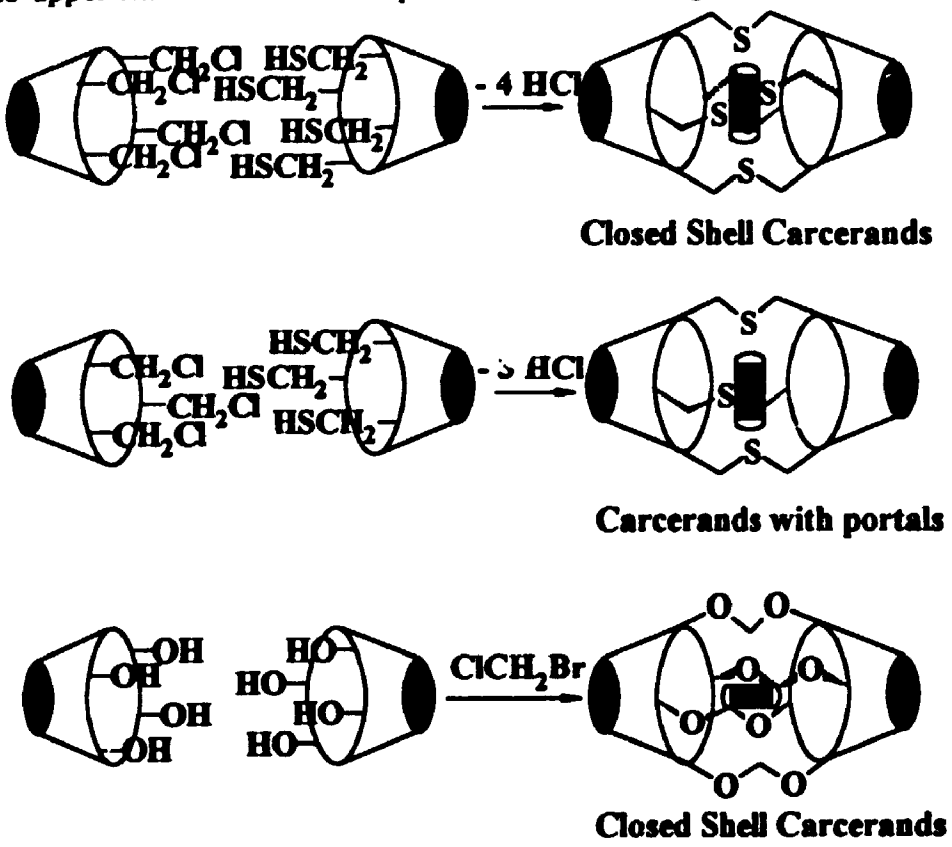


Figure 16. Synthesis of carcerands

Tetraaldehydes, tetraalcohols, tetrachlorides and tetrathiols were synthesized as key intermediates for these more complicated carcerands. By direct condensation of two functionalized cavitands or by condensation of two cavitands with bifunctional reagents like CH_2ClBr under dilute conditions, intramolecular bridging between two cavitands was achieved to give shell closure of two hemispherical cavitands, or carcerands as Figure 16 shows.[2,34,87,94,95]

Various carcerands have been synthesized by Cram and co-workers. When the joining of two cavitands takes place, it creates a large cavity to incarcerate guest molecules present in the reaction medium. These carcerands contain a closed cavity that is large enough to imprison many small molecules. However, there are two different types of carcerands. Some carcerands are closed surface spheres. Once the small guests were admitted into the closed cavity during the synthesis, they were permanently incarcerated even at high temperature and low pressure. Some of the carcerands contain portals in their shells. Through the portals, only larger entities can remain inside of the cavity whereas small molecules such as O_2, N_2, H_2O are able to traverse the pores.[12] With these properties, the carcerands become one of the most powerful complexing agents in supramolecular chemist for many small guest molecules.

1.8 TRANSITION METAL DERIVED CALIXARENES

The transition metal complexes of macrocyclic ligands and their host-guest chemistry have developed rapidly over recent years.[1-8] Transition metal complexes play central roles in such important areas as drug action, enzyme-substrate interactions and enzymatic catalysis. The transition metal ion chemistry of macrocyclic ligands has now become a major subdivision of inorganic chemistry and undoubtedly interest in this area will continue increasing in the near future.

1.8.1 Oxophilic Transition Metal Complexes

Philip Power and his coworkers at University of California at Davis[101] were the first to explore the interaction of calixarenes with transition metal ions in their search for unusual coordination and reactivity patterns. Treatment of *p-tert*-butylcalix[4]arene with $Ti(NMe_2)_4$ gave a product containing two *p-tert*-butylcalixarenes and two Ti atoms. The X-ray structure study indicated that the two titanium atoms were sandwiched by a pair of *p-tert*-butylcalixarene units in the cone conformation as illustrated in Figure 17.

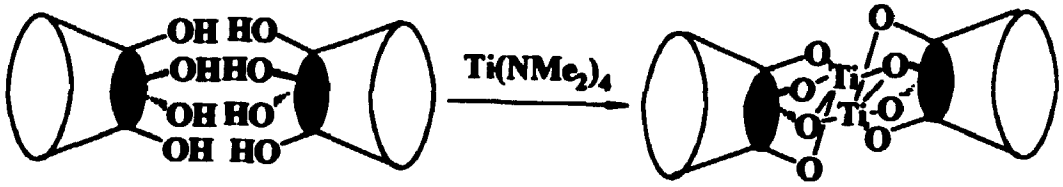


Figure 17. Formation of a titanium complex of *p-tert*-butylcalix[4]arene

In similar fashion, the sandwich complexes, $[Fe(NH_3)(Calixarene\text{-}OSiMe_3)_2]$ and $[Co_3(THF)(Calixarene\text{-}OSiMe_3)_2]$, were obtained when *p-tert*-butylcalixarene was treated with $Fe[N(SiMe_3)_2]_3$ or $Co[N(SiMe_3)_2]_2$ respectively. In spite of small deformations due to the binding of the metal atoms, the two *p-tert*-butylcalix[4]arene units still showed a regular cone conformation. A significant feature observed in these complexes is their ability to form endo complexes with organic solvents. The Ti and Co complexes each included a toluene molecule each inside their intramolecular cavity.[101]

Following that, several other closely related oxophilic transition metal complexes have been reported.[102-106] Atwood and his coworkers have explored the interaction of several calixarene ethers with titanium salts and aluminum alkyls. An especially interesting

complex is formed by the interaction of the tetramethyl ether of *p-tert*-butylcalix[4]arene with Me_3Al to give colourless crystals in which two aluminum atoms fuse two calixarene molecules together.[107] The *p-tert*-butylcalix[8]arene forms a series of metal complexes with the lanthanide ions. The structure revealed by X-ray crystallography contains two europium atoms embedded in a pinched conformer of the cyclic octamer.[108] Andreetti and coworkers treated *p-tert*-butylcalix[6]arene with $Ti(OPr)_4$ and obtained a similar complex Ti_4(*p-tert*-butylcalix[6]arene)$_2$ in which Ti atoms were pentacoordinated in a slightly distorted trigonal bipyramid.[109] Treatment of $MoOCl_4$ with *p-tert*-butylcalix[4]arene could give an oxomolybdenum capped calixarene complex in which the oxomolybdenum(VI) binds four oxygen atoms from the calixarene and one water molecule in its cavity.[102] Similarly, Corazza and coworkers capped the *p-tert*-butylcalix[4]arene with transition metals such as W(VI), Nb(V) and Ta(V) by reacting the *p-tert*-butylcalixarene with $WOCl_4$, $NbCl_5$, or $TaCl_5$ respectively.[102-107]

1.8.2 Later Transition Metal Complexes

Due to the 'soft' properties of later transition metals, direct coordination of later transition metals with oxygen donors seems to be difficult. However, once 'soft' atoms, such as phosphorus and sulfur, are attached to the macrocyclic system, the transition metal can be easily introduced. The *p-tert*-butylcalix[4]arene has been reported to be converted into the corresponding tetra(diphenylphosphinite) derivative by using diphenychlorophosphine in the presence of BuLi as base.[110,111] The reactions of this derivative with Cu(CO)Cl and $[Fe(CO)_3(\eta^2\text{-}C_8H_{14})_2]$ at low temperature led to a polycopper(I) species and a complex

with two $Fe(CO)_3$ units chelated by the phosphinito groups respectively as illustrated in Figure 18.[110,111]

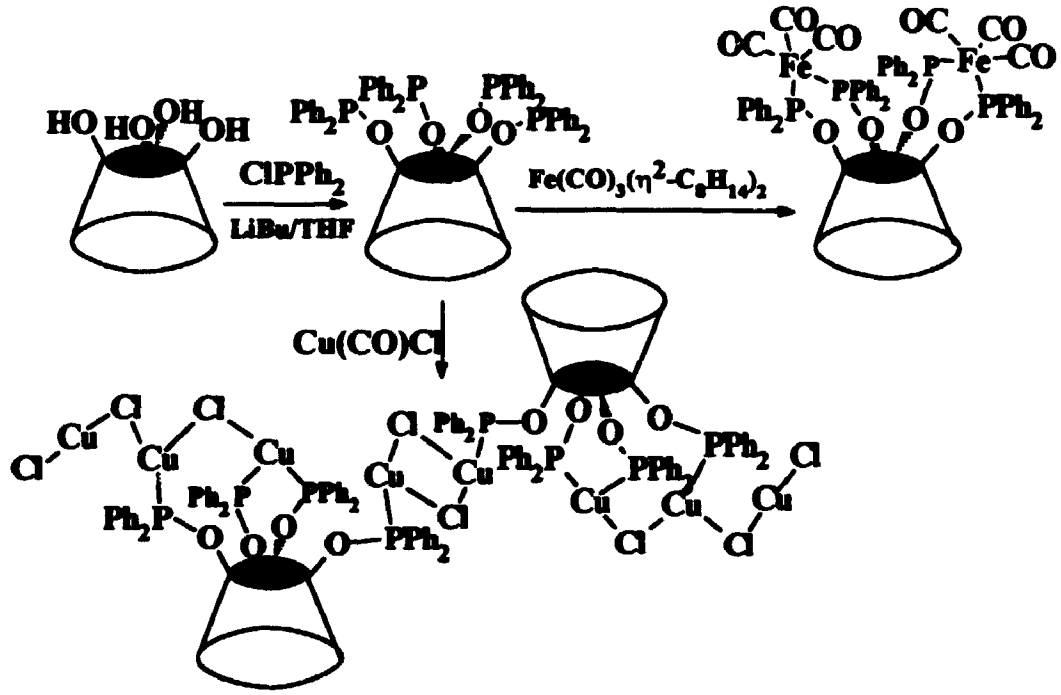


Figure 18. Formation of late transition metal complexes of calixarenes

1.8.3 The Arene Complex $Cr(CO)_3$-Calixarene

It is known that tricarbonylchromium forms stable η^6-arene complexes and that the complexed phenyl ring then becomes extraordinarily reactive. It is expected that the phenyl units in a calixarene will be activated through complexation with $Cr(CO)_3$. Recently, an arene-tricarbonylchromium complex, prepared by interaction of tetrapropoxycalixarene with $Cr(CO)_6$, has been reported. The X-ray structural analysis revealed that two opposite phenyl units of the calixarene each carry a $Cr(CO)_3$ unit on the outside of the calixarene bowl.[112,113]

1.9 GUEST-HOST CHEMISTRY OF CALIXARENES

It is common to speak of hosts as having closed cavities, channels, interlayer spaces and bowl-shaped cavities. The most important factors which affect the selectivity of the inclusion chemistry are the molecular dimensions and the fine interactions between guest and host. One of the most useful properties of calixarenes is their ability to function as molecular receptor and so to bind neutral and ionic guests. The cavities of calixarenes are large enough to form inclusion complexes with many molecules and metal cations, such as water, benzene, toluene, carbon disulphide, dichloromethane, chloroform and both alkali and transition metal cations.[87] Calixarene chemistry is distinguished by the fascinating ability to host various guests.[7,8]

1.9.1 Cation Inclusion

A typical property of crown ether systems is their ability to form stable complexes with the alkali metal and alkaline earth ions. The impetus to the study of such complexes was the recognition of important roles of Na^+, K^+, Mg^{2+} and Ca^{2+} ions in biological systems. Based on the structural resemblance between the crown ethers, cyclodextrins and calixarenes, extensive investigations on the complexation behaviour of calixarenes have been carried out.[3]

1.9.1.1 Alkali Metal Cations: The complexation of alkali and alkaline earth cations by calixarenes has been examined extensively by using phase transfer from water

into an organic solvent, ion transport through liquid membranes and stability constant measurements. Izatt and his coworkers tested the ability of calixarenes to transport cations across a liquid membrane.[114] They found that, although the calixarenes are ineffective cation carriers in neutral solution, they possess transport ability for alkali cations in strongly basic solution, in contrast to 18-crown-6 which is more effective in neutral solution than in basic solution.[114-117] The selectivity is always towards the less hydrated Cs^+, independent of the size of the calixarene ring. Under the same conditions, *p-tert*-butylphenol shows little ability to carry cations and this difference supports the idea that the macrocyclic ring plays a critical role. It is believed that the useful features of calixarenes as ion carriers arise from their low water solubility and their ability to form neutral complexes with cations through the loss of protons. Böhmer suggested that, at least in the case of Cs^+ ion, the transport is by an endo-calix complex which will provide a particularly good environment for a Cs^+ ion after it has lost its hydration shell.[118] The presumption that calixarene carried alkali cations in or near the cavity has received support recently with X-ray analysis of a Cs^+ complex of the *p-tert*-butylcalix[4]arene.[109,119]

Tetraacetate derivatives of *p-tert*-butylcalix[4]arenes, carboalkoxymethyl ethers of *p-tert*-butylcalix[4]arenes and other calixarene 'podands' with keto, ester and amide groups, however, have the highest affinity for Na^+, as is exhibited in both the higher stability constant in MeOH and in the per cent extraction into dichloromethane.[120,121] Two nice examples of such alkali cation inclusion have been revealed by X-ray analysis in which one *p-tert*-butylcalixarene in a partial cone conformation had a Na^+ ion located in the

middle of the cavity[122] and another *p-tert*-butylcalix[4]arene acetamide in the cone conformation encapsulated a K^+ in a cage formed by eight coordinated oxygen atoms [31]

1.9.1.2 Organic Cations: An example of non-aqueous phase complexation that indirectly involves ammonium ions has been reported by Gutsche.[123,124] Small perturbations of both guest and host are observed in the ^1H NMR spectra of mixtures of calix[4]arenes and amines. These observations are explained in terms of a proton transfer from the calixarene to the amine to form a calixarene monoanion and an ammonium cation which then combine to produce what is thought to be an endo-calix complex as shown in Figure 19.[123,124]

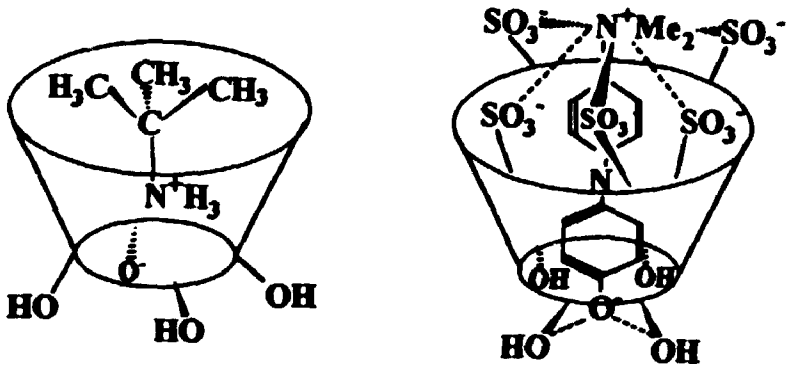


Figure 19. Formation of endo-calix amine complexes

The driving force for inclusion of aliphatic amines by calix[4]arenes in polar solvents is postulated to be a combination of proton transfer and electrostatic attraction.

Water soluble calixarenes are most interesting because of their potential as enzyme mimics. Shinkai et al.[125-129] have studied the aqueous phase complexes. The water

soluble calixarene *p*-sulphonate hosts organic cations, such as phenol blue, benzenediazonium ions, trimethylanilinium ions, in endo-calix style as pictured in Figure 19. They have noted that the complexation is driven by favourable enthalpy changes with calix[4]arenes. By studying the interaction of several quaternary ammonium salts with the water soluble tetra-anion of calixresorcinarene, they also concluded that the electrostatic interaction is the main driving force for organic cation complexation.[130-132]

1.9.1.3 Transition Metal Cations: There has been much interest recently in macrocyclic ligands for use in transition metal cation selective reagents, ion storage and transport in vivo, the solvent extraction of metals, the synthesis of new chromatography materials for separation of metal ions and discrimination between related metal ions based on their relative fit for the cavity of the ligands.

Uranium in sea water exists as the UO_2^{2+} cation. Although the water soluble *p*-sulphonatocalix[4]arene has little complexing ability for UO_2^{2+}, both *p*-sulphonatocalix[5]arene and *p*-sulphonatocalix[6]arene have dramatic selectivities for UO_2^{2+} in preference to other cations such as Ni^{2+}, Zn^{2+} and Cu^{2+}. This is attributed to the geometric requirement for UO_2^{2+} complexation which is pseudoplanar penta- or hex-coordinate in contrast to that of Mg^{2+}, Ni^{2+}, Zn^{2+} and Cu^{2+}, which is square planar or tetrahedral.[133-135] Several other calixarene derivatives bearing carboxyl groups, hydroxamate groups and amide groups on the lower rim have also been reported to show selective extraction of transition metal cations such as Fe^{3+}, Cu^{2+}, Zn^{2+} and Pd^{2+} from the aqueous phase to the organic phase.[136]

1.9.2 Neutral Molecule Inclusion

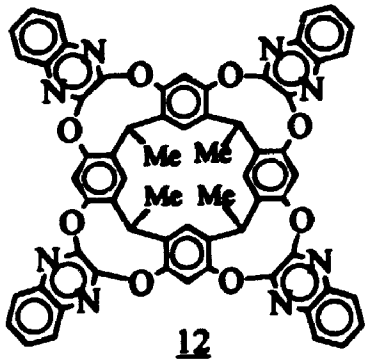
Study of the interaction of the macrocyclic compounds with neutral molecules showed that the arrangement of donor atoms in the macrocyclic framework or recognition site, which can lead to very strong and specific complexation particularly by hydrogen bonding, π-π or σ-π interactions, should play an important role in the selectivity towards guest inclusion.

1.9.2.1 Inclusion in Solution There exist only a few cases of the inclusion of guest molecules by calixarenes in organic media.[6] This lack of examples is because there is a competition between complexation and solvation. However, by using the technique of aromatic solvent-induced shift (ASIS), the interaction of calixarenes with solvent has been studied.[6] With chloroform as the reference solvent, toluene as the guest molecule and a linear tetramer as the reference compound, changes in chemical shifts of various protons were measured as a function of the chloroform:toluene ratio. An approximately linear relationship was observed and was interpreted in terms of formation of a 1:1 complex. The ASIS studies indicated that the calix[4]arene forms complexes with both toluene and chloroform with little selectivity. Attempts to demonstrate complex formation with other guests have not been successful, probably because the solvent molecules are too effectively complexed with the host.

1.9.2.2 Inclusion in the Solid State: It is well known that calixarenes show an ability to retain the solvent from which they are crystallized. The X-ray crystal structure

of the first endo cavity complex was reported by Andreetti (Figure 3). Since then, a number of structures in which a calixarene hosts small molecules have been determined by X-ray crystallography.[44,29,137-139] The formation of solid-state endo-calix complexes was observed with chloroform,[140] benzene,[141] toluene,[29] xylene,[141] acetonitrile,[142] anisole,[141] and several other guests.[143] A rough estimation of the strength of these adducts can be obtained by the observation of their macroscopic behaviour. Normally, the binding strength of a guest decreases with an increase on the cavity size of the host. For example, endo-calix complexes of *p-tert*-butylcalix[4]arene with benzene, toluene, xylene and anisole are stable at room temperature whereas the chloroform complex of *p-tert*-butylcalix[8]arene loses chloroform in a few seconds and the chloroform complex of *p-tert*-butylcalix[6]arenes is stable and retains chloroform even after heating at 257°C and 1 mm-Hg pressure for six days.

Another interesting example of endo-complex with acetone is offered by the 1,4-diazanaphthalene-cavitand **12** which has a deeper cavity than that present in other cavitands. The cavitand **12** housed two acetone molecules in its cavity.[144]



12

1,4-Diazanaphthalene-Cavitand

1.10 POTENTIAL INDUSTRIAL APPLICATIONS OF CALIXARENES

Von Böyer developed commercially the phenolic resins used in bakelite. Scientists in several countries are now looking for applications for the calixarenes.[145] One of the first applications was that of the Petrolite Company in the US in 1950 which marketed the product of O-alkylation of *p-tert*-butylphenol formaldehyde oligomers as surfactants with excellent deemulsifying properties. Most of the recent applications of calixarenes were associated with their properties as molecular receptors.[9,146,147]

1.10.1 Applications in Analytical Chemistry

Analytical applications have been focused on uses as sensors and in chromatography. The most successful sensor application involved using calix[4]arenes to make PVC membranes which showed remarkable Na^+ selectivity.[148] This material has been used to make Na^+ selective electrodes and a Na^+ detector for flow injection analysis (FIA).[149] These devices have been used to determine Na^+ in human blood plasma and the results showed excellent agreement with those obtained from laboratory analyzers.[150] Ion-selective electrodes for K^+ and Cs^+ have been successfully made using dioxacalix[4]arene as the ionophore.[151] Ion selective field effect transistors (ISFET) containing a calixspherand as the ionophore enable a quantitative determination of K^+ in the presence of a large excess of Na^+. A recent approach was to include the calixarene-based sensor with several others in an array of sensors. This approach gave very accurate assays for sodium and other ions in blood and mineral waters.[152,153]

Calix[4]arenes containing S and/or N donor atoms could selectively bind environmentally important heavy metal ions, such as Ag^{+}, Hg^{2+}, Cd^{2+}, Pb^{2+} and Cu^{2+}.[154] The calix[4]arene-based ion-selective electrodes are now being developed.[156] By applying chemically modified electrodes with calix[4]arene derivatives bound onto the surface, it was possible to determine Pb^{2+}, Ag^{+} and Cu^{2+} ions simultaneously by using differential pulse anodic stripping voltammetry.

Some applications in chromatography, including the use of *p-tert*-butylcalix[8]arene as a stationary phase in gas chromatography for separating alcohols, chlorinated hydrocarbons and aromatics, have been reported.[9]

Various chromogenic,[157] fluorogenic[158] and light-switchable ionophores[159] containing calixarene derivatives will open further possibilities in calixarene applications. Resorcinol-based calixarenes showed strong and specific interactions via hydrogen bonding with certain sugars. This interaction may lead to specific sensors.[160]

1.10.2 Applications in Material Science

As we mentioned before, both the thermal and air stable properties of calixarenes will lead to many applications in material science.

1.10.2.1 Liquid Crystalline Materials and Materials with Non-linear Optical Properties: New liquid crystalline materials have been obtained from tungsten-capped

calix[4]arenes.[161] The *p*-nitro and *p*-$OC(O)C_nH_{2n+1}$ (n=9-21) calixarene ether derivatives show non-linear optical properties useful for frequency doubling of laser light.[162,163]

1.10.2.2 Stabilizers for Organic Polymers: The thermally stable and non volatile nature of calixarenes allowed their use as antioxidants for organic polymers. Seiffarth et al have shown that the calixarenes were efficient inhibitors of polyolefin oxidation. This is probably because calixarenes form relatively stable phenoxy-type radicals which prevent propagation of radical chain reactions.[164]

1.10.2.3 Accelerators for Instant Adhesives: Several patents claimed the use of certain modified calixarenes as accelerants for cyanoacrylate instant adhesives to reduce fixation times and make more durable bonds.[165,166]

1.10.2.4 Langmuir-Blodgett Films and Membranes: Monolayer films have been successfully made with several calixarenes.[167,168] The acetate of *p*-methylcalix[6]arene is particularly interesting because it exhibited the highest solubility in various organic solvents with heat resistant film up to 400°C.[169] The latter technique has also been used to produce perforated monolayers leading to membranes with permeabilities defined on the molecular level.[170,171]

1.10.2.5. Catalysts: Since the calixarene could include the metal ions inside their cavity, they would enhance the solubility of a range of metal salts in organic solvents as phase-transfer catalysts and leave "naked" anions outside which may become more

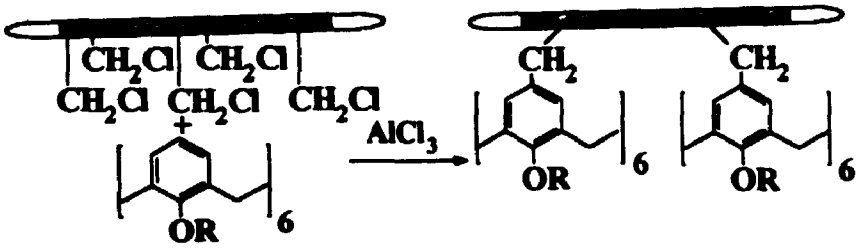
effective nucleophiles. The calixarene was found to improve significantly the yields of products of the nucleophilic displacement of bromide in phenacyl bromide by acetate or by azide in acetonitrile.[172] Several authors have shown the catalytic properties of calixarenes in hydrolysis reactions.[129,173] The results presented in Table 1 suggested that the calixarenes can be used as catalysts for nucleophilic reactions. Shinkai[174] and Gutsche[175] have studied the acid-catalyzed addition of water to 1-benzyl-1,4-dihydronicotinamide in the presence of calixarenes. They found that the p-sulphonatocalix[6]arene is a better catalyst than other calixarene derivatives. When the lower rim of the calixarene was modified with $O(CH_2CH_2O)_mMe$ (m = 1-3) it showed catalytic activity comparable with dicyclohexyl-18-crown-6.[176]

Table 1. Catalytic properties of calixarenes

Reactions	% of Calixarene	Yield
$PhC(O)CH_2Br \xrightarrow{KOAc} PhC(O)CH_2OC(O)CH_3$	0	0%
$PhC(O)CH_2Br \xrightarrow{NaN_3} PhC(O)CH_2N_3$	6	95%

1.10.2.6 Polymeric Calixarenes: Calixarene containing polymers can be achieved by either attaching the calixarene to a support polymer or by polymerizing calixarene itself by introducing proper functional groups as illustrated in Figure 20.[125,177] Methacrylate calix[4]arene can be polymerized under free radical conditions to give a polymer with a molecular weight of ca. 6745. The polymer can form stable complexes with NaCNS.[178]

Route I. Attach Calixarenes to Functionalized Polymers



Route II. Polymerization of Functionalized Calixarenes

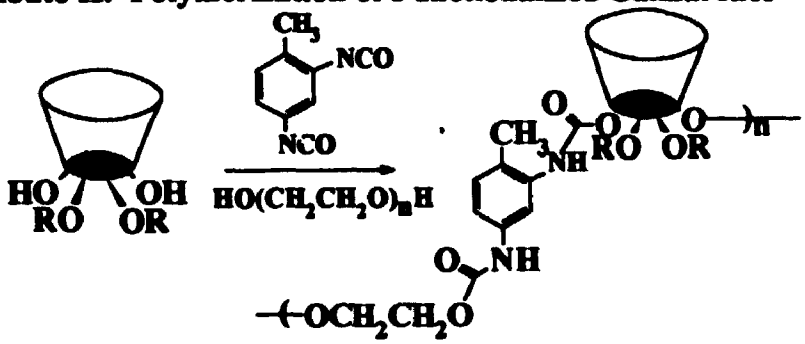


Figure 20. Calixarene containing polymers

These polymers have been claimed as adsorbents for heavy metal ions[179] and as catalysts.[180] Two more patents were issued to Hitachi Chemical Co., Ltd in 1987 describing polymeric calixarenes that are stated to have good metal absorptivity and heat resistance. They were derived from *p*-phenylcalixarenes by acylation with RCOCl (R = $CH{=}CH_2$, $C(Me){=}CH_2$) which introduces unsaturated acyl groups into the 4'-position of the biphenyl ring. Polymerization in the presence of methyl methacrylate was induced with AIBN to give a copolymer with a softening point at 180-185°C.

1.10.3 Molecular and Metal Cation Receptors

1.10.3.1 Recovery of Cesium: The recovery of caesium is the oldest

application of supramolecular chemistry. Several patents have been filed on a process for recovering metallic cations from solutions of nuclear waste materials on the principle that the transport rate for Cs^+ is about 100 times higher than for K^+, Na^+ and Li^+ and six times higher than for Rb^+.[181,182]

1.10.3.2 Recovery of Uranium: The world's oceans contain a total of about 3 billion tons of uranium, present as UO_2^{2+} in association with carbonate. However, extraction of uranium from sea water is difficult due to its dilute concentration (about 3 parts per billion) and since numerous other cations are present in larger concentration. A polymer-bound material, in which the hexakis(carbethoxymethyl)ether of *p*-sulphonatocalix[6]arene was partially nitrated, aminated and fixed on crosslinked chloromethylated polystyrene, was stated to absorb 108μg of uranium from sea water per 0.1g of the material in seven days at a flow rate of 30mL/min.[64] It was clear that only *p*-sulphonatocalix[n]arenes (n=5-6) showed strong specific complexation to uranium and can extract uranium from seawater or nuclear wastes.[6,9,134,183]

1.10.3.3 Lanthanide Sequestration: Harrowfield et al have reported that *p-tert*-butylcalix[8]arene provided a ready means of converting all the lanthanides to organic solvent soluble complexes and suggesting that *p-tert*-butylcalix[8]arene might be used in the purification of the lanthanides[184]

1.10.3.4 Separation of Neutral Organic Molecules: The extraction of aryl compounds with calixarenes has been reported. The most striking results were their

selectivity. For example, the *p*-isopropylcalix[4]arene could extract p-xylene selectively and *p*-isopropylbishomooxacalix[4]arene showed specificity to o-xylene.[124,185]

The organic solvent extraction properties of the calixarenes can also be used in environmental chemistry as organic solvent collectors to control water pollution. In a recent patent, Wainwright proposed a method for the removal of organic compounds, particularly polar hydrocarbons such as halogenated hydrocarbons, with non-solvated calixarene compounds.[186]

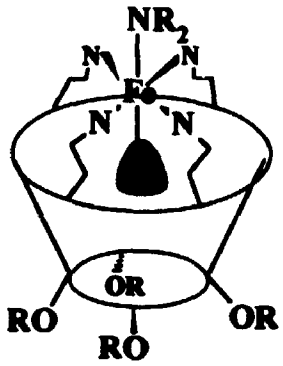


Figure 21. Heme mimic of *p*-(2-aminoethyl)calix[4]arene

1.10.4 Biomimics

A major reason for interest in calixarenes is their potential to mimic various natural systems. Porphyrin-iron complexes are well known to bind oxygen reversibly. In the hope of developing a non-porphyrin heme mimic, *p*-(2-aminoethyl)calix[4]arene has been synthesized.[180] The compounds containing four aminoethyl groups can bind transition metal cations, such as Fe^{2+}, Cu^{2+} and Ni^{2+} in a square planar fashion, leaving a potential

coordination site on the metal towards the center of the bowl. The empty coordination site is only accessible to small molecules which can transfer through the annulus of the calixarene as illustrated in Figure 21.

1.11 CONCLUSIONS

Three advantages of calixarenes over other synthetic macrocycles in host-guest chemistry are:

(1) the calixarenes can be synthesized on a large scale and in good yields,

(2) the calixarenes have adjustable cavity sizes and

(3) the calixarenes can be functionalized easily and selectively both at the bottom rim and the upper rim.

These advantages bring a particular charm for calixarene chemistry. In the field of molecular inclusion, calixarenes have provided a tool to explore and evaluate weak intermolecular interactions. For cation complexation, calixarenes could act as receptors with unusual efficiency and selectivity. The calixarene chemistry has now established a place in supramolecular chemistry along with the cyclodextrins, crown ethers and cryptands. However, host-guest or supramolecular chemistry is becoming more demanding. Within this context, calixarenes will probably generate even more interest in the near future.

1.12 SCOPE OF THE THESIS

An important goal in modern biochemistry concerns the design of synthetic molecules that mimic various aspects of enzyme chemistry. It was reported that anionic substrates participated in approximately 70% of all enzymatic reactions. It is quite surprising to note that, compared to cation complexation, anion complexation has received very little attention, although anion complexation plays important roles in organic, inorganic and biological chemistry. Therefore, the primary goal of the research is to establish a synthetic model system for anion inclusion and then further study the properties of the included anions and the 'naked cation' chemistry.

1.13 ORGANIZATION OF THE THESIS

The thesis is divided into five sections. Section I, or chapter 1, provides an introduction of the supramolecular chemistry of calixarenes. Section II, which consists of chapters 2 and 3, deals with the design and the synthesis of transition metal rimmed anion acceptors. Section III comprises chapter 4 and 5 and deals with the design and synthesis of metal cation receptors. Section IV, chapter 6 studies the host-guest chemistry of bottom rimmed transition metal calixarenes. Section V, or chapter 7, discusses the influence of transition metal binding on the conformations of the calixarenes. Finally, a brief summary of the achievements made in the course of the study are summarized in chapter 8.

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Chapter Two

TRANSITION METAL RIMMED-CALIXRESORCINARENE COMPLEXES

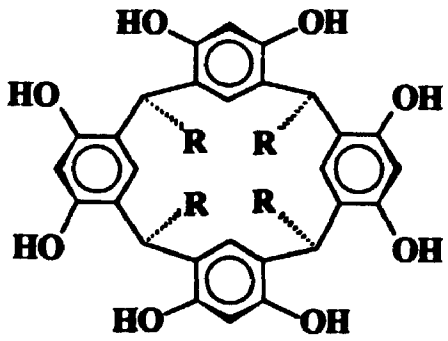
2.1 INTRODUCTION

One strategy for making use of host-guest chemistry for shape and /or size selective catalysis is to derivatize the host molecule with transition metal atoms capable of catalytic activation of guest molecules and this has led to increasing interest in transition metal complexes of macrocyclic ligands.[1-3] The calixresorcinarenes 1, which are easily prepared by condensation of resorcinol with various aldehydes,[4] are bowl shaped compounds that can serve as hosts for small guest molecules and cations.[5-7] This chapter will discuss details of the successful derivatization of the calixresorcinarene to give a phosphonito-cavitand 2 with four PhP units and a phosphinito-calixresorcinarene 3 with eight PPh_2 units around its upper-rim. The strong coordinating ability of 2 and 3 made it possible to introduce transition metals, such as Au, Pt, Rh and Ir to the upper-rim of the calixresorcinarene to give transition metal-rimmed bowl complexes, which have the potential to accept small guest molecules and ions or to function as active catalytic centres.

2.2 RESULTS AND DISCUSSION

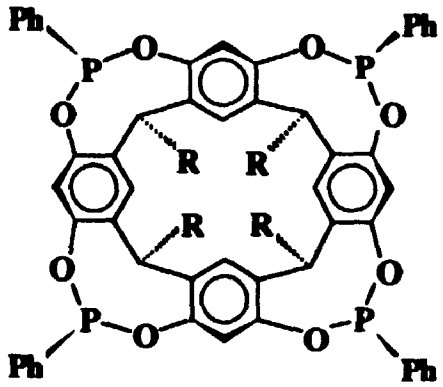
2.2.1. Preparation and Characterization of Phosphonito Derived Cavitand, 2

Although the OH groups[1-2] and aryl rings[8] of a calixresorcinarene can act as coordination sites, the introduction of soft donors, such as phosphorus(III) or sulphur(II) is highly desirable if late transition metals are to be strongly bound to the macrocyclic system. Thus, treatment of the resorcinol-derived calixresorcinarene 1, which has a frozen cone conformation, with phenylphosphonous chloride in the presence of pyridine as base, gave a new phosphorus(III) calixresorcinarene derivative, or phosphonito-cavitand 2. All the spectroscopic data indicate that 2 maintains the cone conformation and so has a bowl-shaped architecture with a deeper cavity than its precursor 1 as shown in Figure 1.



R = CH_2CH_2Ph

1



R = CH_2CH_2Ph

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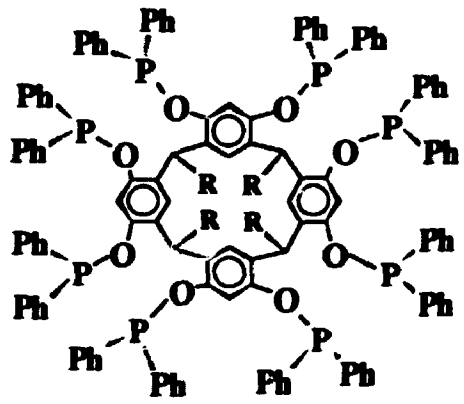


R = CH_2CH_2Ph

3

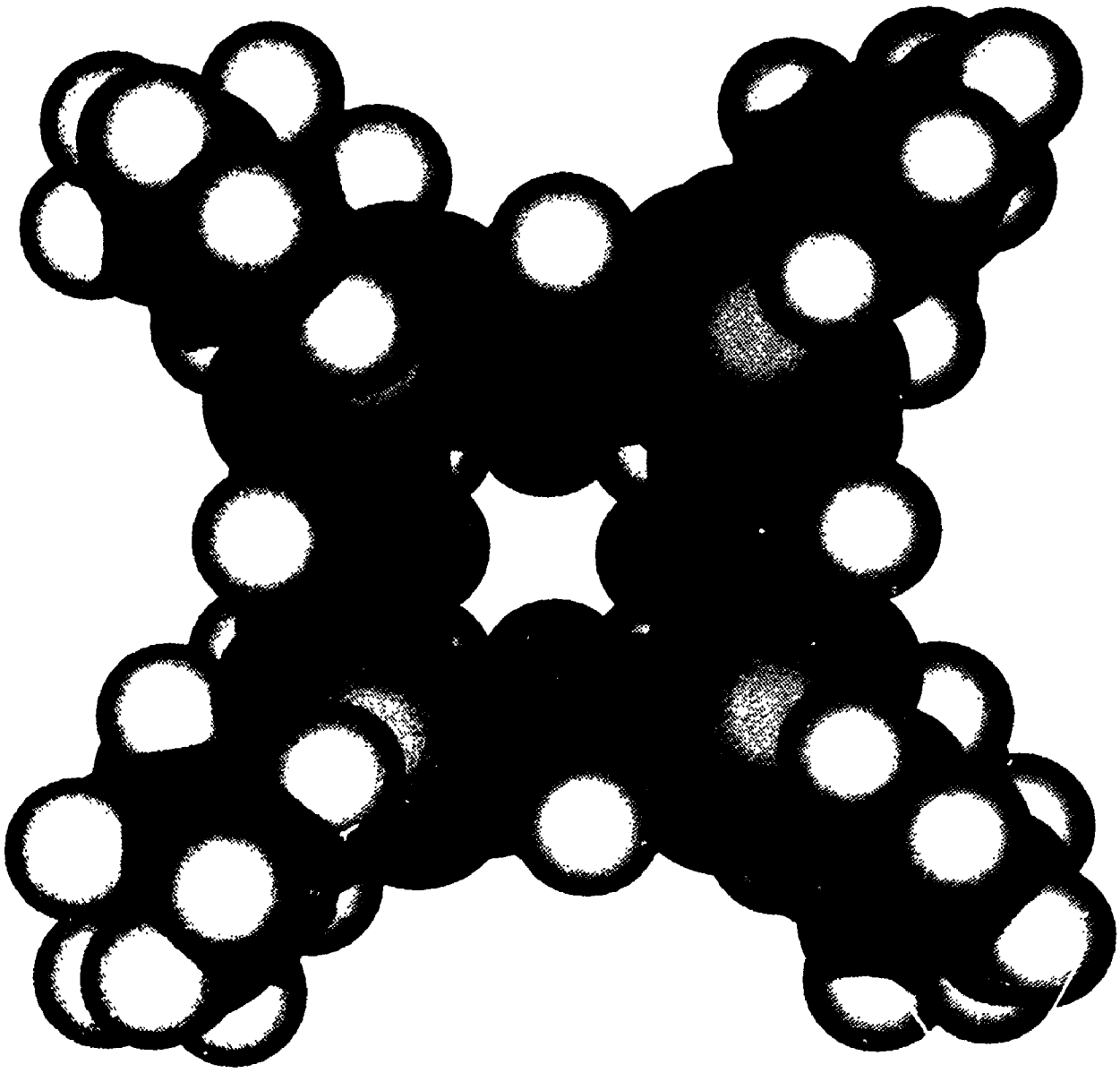


Figure 1 Space filling model of phosphonito-cavitand **2**

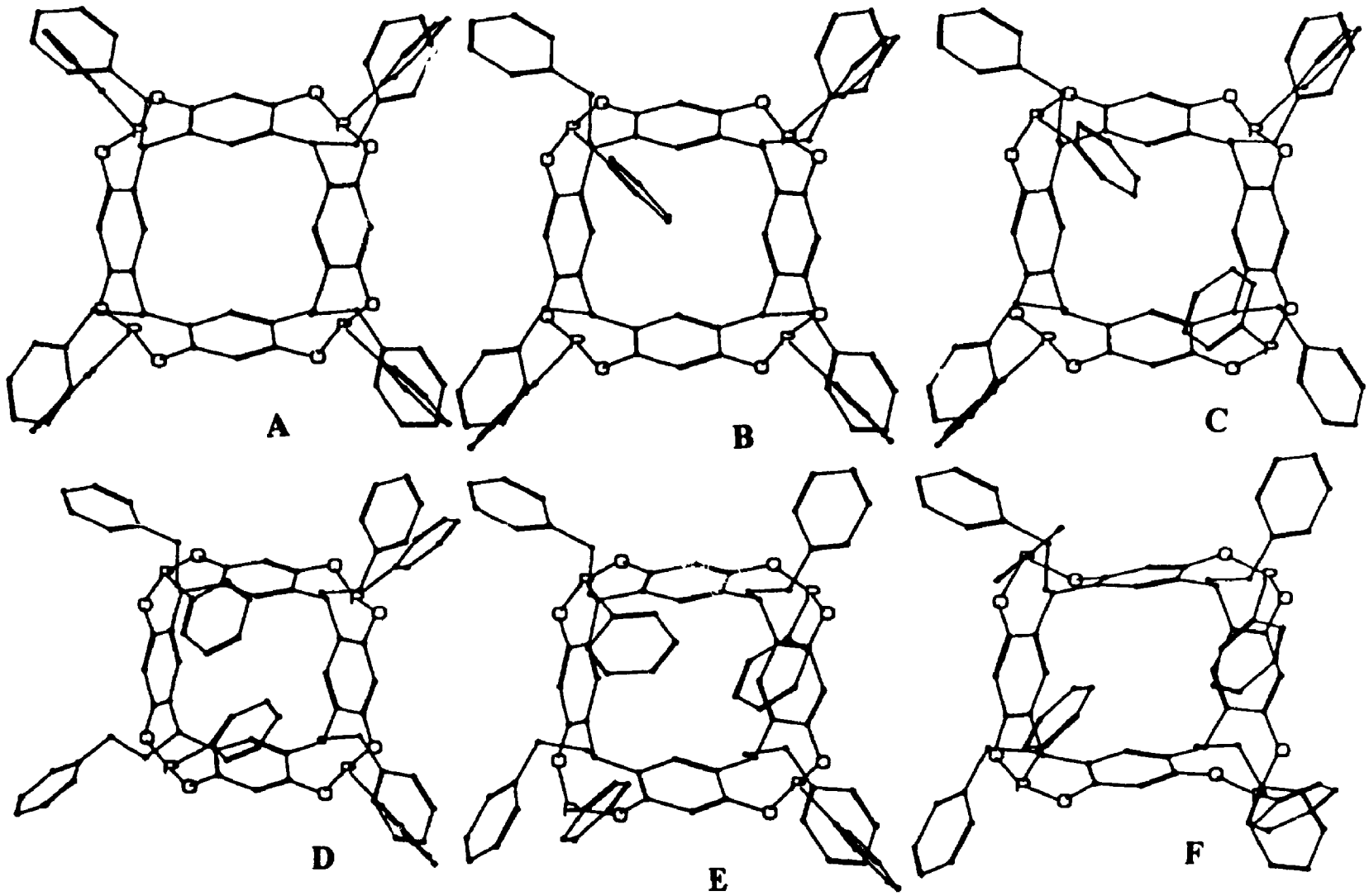


Figure 2. Structures of six possible conformers of compound 2 in their lowest energy conformations (The structures were generated by PCModel program after global energy minimization)

Table 1. Molecular mechanics calculations for the six possible conformers of **2** and Four Possible Isomers of **9**

Compound **2**	A	B	C (trans)	D (cis)	E	F
E	126.61	134.12	146.32	148.41	149.60	153.21
ΔE	0.00	7.51	19.71	21.80	22.99	26.60

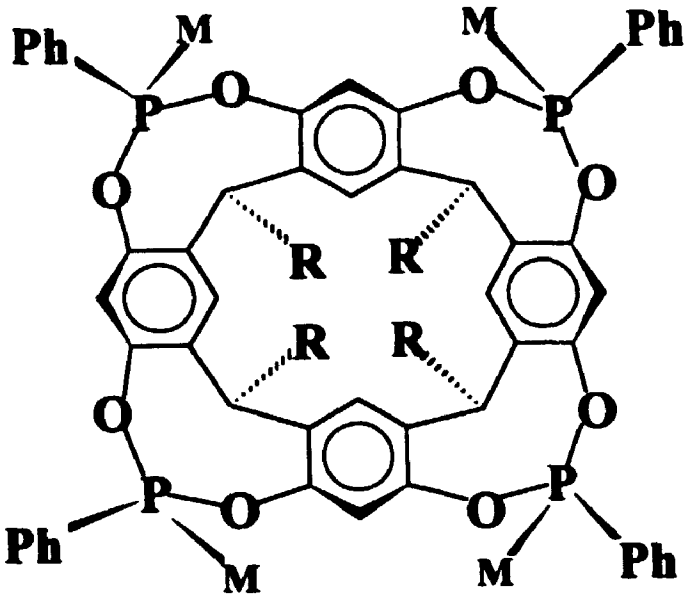
E: MMX Energy; $\Delta E = (E_i - E_A)$ (i = B - F)

However, it should be noted that there are six possible isomeric forms for the cavitand **2**, even when it is in the cone conformation. The lone pair of electrons on the phosphorus atoms of **2** could be directed either outward or inward with respect to the middle of the bowl (Figure 2). Molecular mechanics calculations[9] (Table 1) indicated that the isomer with all phenyl groups directed outwards and lone pairs directed inwards would be preferred and this stereochemistry is consistent with the observation of a single ^{31}P NMR resonance for **2** and with all the chemistry described below.

2.2.2. Gold Rimmed Cavitands

The space filling model of **2** indicates that it has a deeper cavity than its precursor **1** (Figure 1), and so it should have a strong ability to engulf guests. However, the phosphorus donors in compound **2** are too far apart (~6.6Å) to chelate to metals and so they can only act as terminal ligands to transition metals. Thus, treatment of **2** with [AuCl(SMe_2)] gave **4**, by replacement of SMe_2 ligands on gold by the phosphorus donors of **2**. The ^{31}P NMR spectra of **4** contained only one resonance, consistent with the expected stereochemistry with all phenyl groups directed outwards and all AuX groups

inwards.



$R = CH_2CH_2Ph$

$M = AuX$, 4 (X = Cl, Br, I)

$M = PtCl_2(SMe_2)$, 5

The proposed structure was confirmed by an X-ray structure determination of complex **4**.0.5CH_2Cl_2.2.5CH_3CN.H_2O. The structure of **4** is shown in Figure 3 and the selected bond distances and angles are listed in Table 2. The "bowl" is in the conformation predicted by the MMX calculation, namely that with all phenyl groups directed outwards from the centre of the bowl. Each phosphorus is a member of an 8-membered PO_2C_5 ring and these rings adopt an extended chair conformation. Each gold(I) centre is two coordinated with slightly distorted linear PAuCl coordination. Three of the AuCl units

form a "picket fence" around the upper rim of the calixresorcinarene bowl while the fourth AuCl unit is folded into the centre of the bowl and so occupies the cavity normally available to a guest molecule. As a result, the solvent molecules can only occupy regions of space between and not inside the potential host molecules. The P-Au-Cl units are all somewhat distorted from linearity [range of angles P-Au-Cl = 164.2(2) - 167.7(2)°], apparently as a result of repulsive interactions between different AuCl units. For example, the shortest non-bonded Au...Cl distance is Au(3)...Cl(2)= 3.359(8)Å and the repulsive interaction on Cl(2) leads to the angle P(2)-Au(2)-Cl(2) = 164.2(2)°. The geometry imposed by the ligand prevents close Au...Au contacts of the kind commonly observed in gold(I) complexes. In the natural geometry of the bowl ligand, the four AuCl units would collide above the centre of the bowl and so the molecule must distort to avoid this situation. This leads to several unusual bond angles in the complex. As mentioned, the Au(3)Cl(3) group folds into the centre of the bowl and this gives rise to a large angle Au(3)-P(3)-C(311) = 125.3(5)°. The Au(2)Cl(2) and Au(4)Cl(4) units lean towards the vacant space above Au(3) and this causes large angles Au(2)-P(2)-O(3) =123.2(6)°, P(2)-O(2)-C(22) = 125(1)°. The Au(1)Cl(1) group leans towards Au(2) and so the larger angles are Au(1)-P(1)-O(1) = 122.6(5)° and P(1)-O(1)-C(12) = 131(1)°. The range of angles Au-P-O = 110.1(5)-123.2(6)°, Au-P-C = 115(1)-131(1)° emphasizes the extent of these distortions. The geometry of the $PhPO_2$ units is much more constant as shown by the much narrower range of angles O-P-O = 103.2(7)-105.7(7)° and O-P-C(Ph) = 99.7(7)-101.7(7)°.

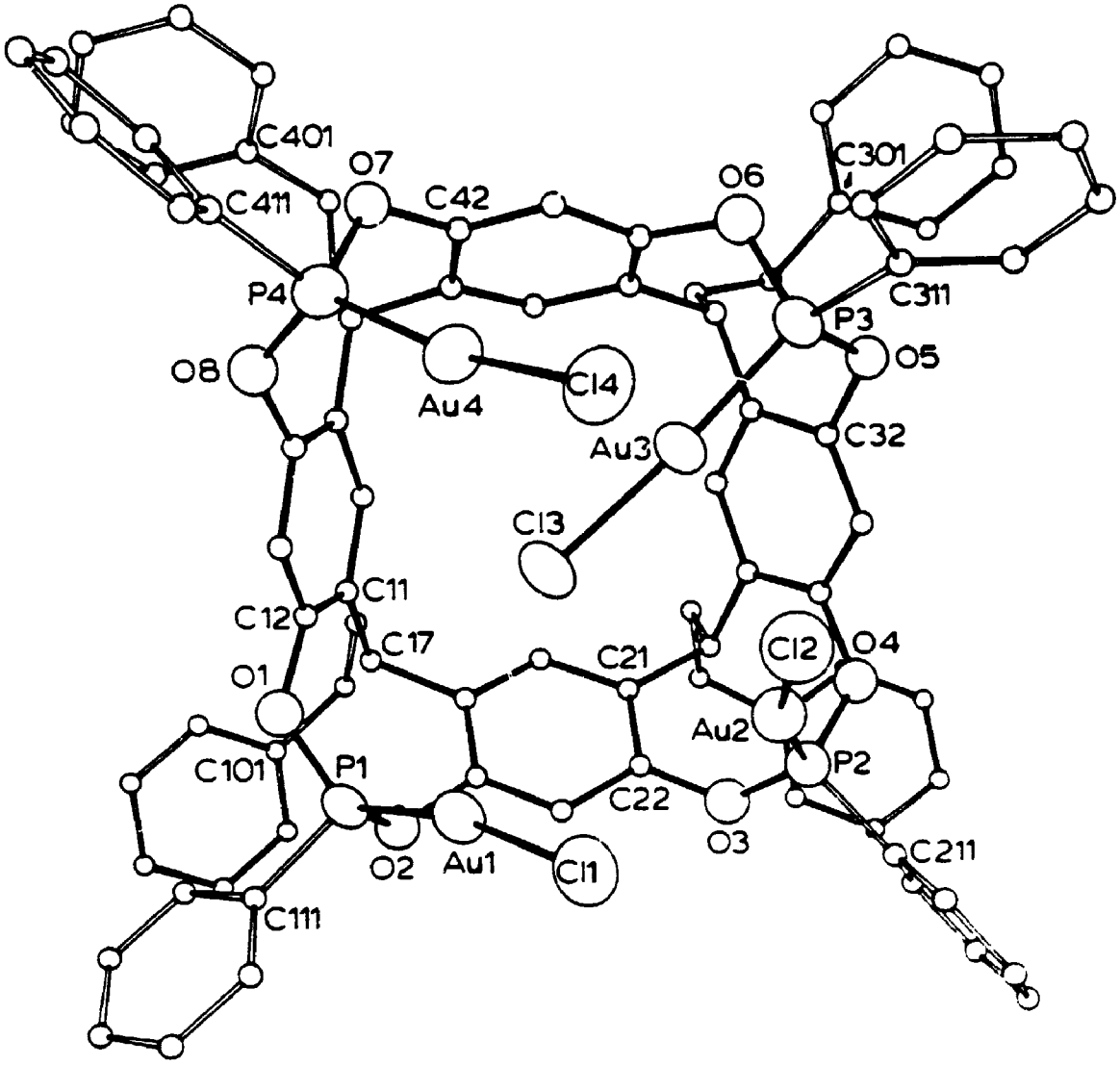


Figure 3. **A top view of the structure of gold complex 4a**

Table 2. Selected bond distances (Å) and angles (°) for **4a**

(a) Bond distances (Å)

Au(1) - Cl(1)	2.270(6)	Au(2) - Cl(2)	2.295(6)	Au(3) - Cl(3)	2.297(6)
Au(4) - Cl(4)	2.291(6)	Au(1) - P(1)	2.212(6)	Au(2) - P(2)	2.191(6)
Au(3) - P(3)	2.223(6)	Au(4) - P(4)	2.210(6)	P(1) - O(1)	1.59(1)
P(1) - O(2)	1.62(1)	P(2) - O(3)	1.60(1)	P(2) - O(4)	1.63(1)
P(3) - O(5)	1.60(1)	P(3) - O(6)	1.61(1)	P(4) - O(7)	1.63(1)
P(4) - O(8)	1.60(1)	P(1) - C(111)	1.77(2)	P(2) - C(211)	1.79(2)
P(3) - C(311)	1.75(2)	P(4) - C(411)	1.76(1)	O(1) - C(12)	1.42(2)
O(2) - C(24)	1.40(2)	O(3) - C(22)	1.38(2)	O(4) - C(34)	1.39(2)
O(5) - C(32)	1.43(2)	O(6) - C(44)	1.41(2)	O(7) - C(42)	1.38(2)
O(8) - C(14)	1.40(2)				

(b) Bond angles (°)

Cl(1) - Au(1) - P(1)	166.9(2)	Cl(2) - Au(2) - P(2)	164.2(2)
Cl(3) - Au(3) - P(3)	167.7(2)	Cl(4) - Au(4) - P(4)	166.6(2)
Au(1) - P(1) - O(1)	122.6(5)	Au(1) - P(1) - O(2)	110.1(5)
Au(2) - P(2) - O(3)	123 2(6)	Au(2) - P(2) - O(4)	110.2(5)
Au(3) - P(3) - O(5)	111.9(5)	Au(3) - P(3) - O(6)	110.8(5)
Au(4) - P(4) - O(7)	111.4(5)	Au(4) - P(4) - O(8)	122.6(6)
Au(1) - P(1) - C(111)	114.9(5)	Au(2) - P(2) - C(211)	116.7(5)
Au(3) - P(3) - C(311)	125.3(5)	Au(4) - P(4) - C(411)	115.1(5)

Since all PAuCl units are equivalent on the NMR time scale even at -80°C, it is clear that the Au(3)Cl(3) unit can easily move to the periphery of the bowl and so exchange with the other AuCl units. A structure with no AuCl unit folded into the bowl would require more twisting of the AuCl units and probably a flattening of the bowl structure. In such a conformation, small guest molecules could be admitted. Attempts to modify the complex with other anions such as $CCPh^-$, NO_3^- and CN^- were unsuccessful.

2.2.3. Platinum, Rhodium and Iridium Rimmed Cavitands

The ligand **2** reacted with four equivalents of $[PtCl_2(SMe_2)_2]$, with displacement of only one SMe_2 ligand from each platinum atom, to give **5**. Complex **5** has effective C_4 symmetry, as shown by the presence of a single resonance in the ^{31}P NMR spectrum. The presence of a single phosphorus donor on each platinum in **5** was most easily demonstrated by recording the ^{195}Pt NMR spectrum, which appeared as doublet due to the coupling $^1J(PtP) = 4966Hz$. The remaining SMe_2 ligand was readily identified in the ^1H NMR spectrum by a singlet with satellites due to coupling to ^{195}Pt with $^3J(PtH) = 52Hz$, and the magnitude of this coupling shows that the SMe_2 ligand is trans to chloride rather than phosphorus. Hence each platinum is shown to have the cis-$Pt(SMe_2)Cl_2P$ coordination.[10] This reaction illustrates clearly that the ligand **2** cannot chelate to platinum(II). Complex **5** is expected to have significant steric hindrance between the $PtCl_2(SMe_2)$ units and so a greater degree of distortion of the natural bowl geometry is expected compared to **4**.

The Rh(I) complexes, such as $[RhClPPh_3)_3]$ and $[RhCl(CO)(PMe_3)_2]$, are active homogeneous catalysts for an amazing variety of organic reactions like hydrogenation, isomerisation and hydroformylation. Phosphine ligands have played a dominant role in the development of new homogeneous catalysts based on rhodium chemistry.[11] The geometrical effects imposed by macrocyclic ligands on the activity of catalysts have been of interest to many chemists.[12] Thus, treatment of **2** with $[Rh(CO)_2Cl]_2$ in CH_2Cl_2 in inert atmosphere easily gave a product **6**, [**2**.$(Rh(CO)Cl)_4$], with evolution of CO. The ^{31}P NMR spectrum of **6** contained only one doublet resonance due to $^{103}Rh(I)$ coupling and this implies that complex **6** also has effective C_4 symmetry. The phosphorus donors in

compound **2** are too far apart to chelate to the rhodium atoms. The IR spectrum of **6** contains one strong ν_{CO} band at 2009cm^{-1}. This is consistent with the proposed symmetrical configuration.[13] However, based on these spectral properties and on the geometrical requirements imposed by the rigid macrocyclic compound **2**, the exact structure of the $Rh_4Cl_4(CO)_4$ aggregate which caps the top of the bowl is still not clear.[14] Attempts at crystallization of **6** were unsuccessful and further discussion on its structure is not justified.

Complex **6** is air stable even in the solution state and is also inert to reactions with several small molecules, such as H_2 and HCCH which react easily with most phosphine Rh(I) compiexes.[15] Complex **6** had no catalytic activity in hydrogenation of the cyclohexene and n-octene and in the photochemical hydroformylation of benzene.

Similarly, when $[Ir(COD)Cl]_2$ was treated with compound **2**, it gave complex **7** by replacement of one end of the COD ligands on iridium by the phosphorus donors of **2**. The η^2-coordinated COD was clearly identified by its ^{1}H NMR spectrum which showed both coordinated alkene protons at δ = 3.2 and free alkene protons at δ = 5.5. The observation of a single resonance in the ^{31}P NMR spectrum supports a similar symmetric structure as in the Rh(I) complex **6**.

2.2.4. Guest-Host Properties of the Transition Metal Rimmed Cavitands

The selective recognition of biogenic amines is of fundamental interest in biomimetic

chemistry.[11] A primary aim has been the design and synthesis of functionalized macrocycles which can recognize or show catalytic activity towards biologically interesting ammonium guests.[12-14] The host-guest interaction in most organic systems is assumed to be due mainly to the complexation through N-H ... O=C(host) hydrogen bonds and RNH_3^+ ... O=C(host) charge-dipole interactions. These are not possible with the host compounds studied here and another type of interaction will be proposed.

Attempts to find simple organic guest molecules that form endo-calix complexes with **4** were unsuccessful because the potential guests, such as PhCN, MeCN, PhCCH, HCCH, Bu^{t}CCH, do not form complexes which were detectable by spectroscopic methods.[6] It is possible that the AuCl which folds inside could block access into the cavity or that binding is too weak to give selective inclusion in competition with inclusion of solvent molecules, such as $CDCl_3$ or CD_2Cl_2.[6] However, amines, which are expected to have a stronger interaction with gold were proved to be admitted into the bowl as guests. The ^1H NMR spectra of a mixture of **4** and RNH_2 are significantly different from those of the pure host and guest compounds. All guest ^1H NMR peaks broadened because of the fast exchange between intra- and extra-bowl guest molecules. The chemical shift of the NH_2 protons drifted to low field and the shifts were even greater than that induced by protonation to give $\mathbf{RNH_3^+}$. It is implied that the guest not only donates its lone pair to one or more gold(I) atoms in **4** but that the chemical shift is also influenced by ring shielding effects in the macrocyclic cavity. Furthermore, when $\mathbf{RNH_3^+}$ (R = n-Bu and n-Pr) was used as potential guest, no obvious chemical shift changes were observed for either guest or host molecules indicating that no inclusion complex was formed. It is

suggested based on their ^{1}H NMR spectra that the amine was included in **4** as shown in Figure 4. Thus, for an amine with the skeleton $C^1C^2C^3C^4NH_2$, the protons on C^4 are located in the deshielding area generated by the calixresorcinarene phenyl ring whereas protons on C^1 to C^3 extend into the shielding area. When using an amine with a bulky R group, only external complexes are formed with only minor chemical shift changes in the ^{1}H NMR spectra for either the guest or host molecules (Table 3). This is consistent with the model proposed since bulky alkyl groups cannot gain access to the cavity but could still form external complexes.

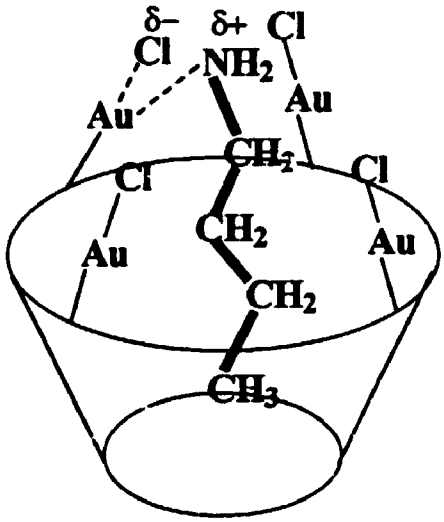


Figure 4. Proposed nature of amine inclusion by gold complex, **4a**

Table 3. Amine inclusion by host complex **4a**

Guest	^{1}H NMR spectra data (ppm) (Chemical shift data for the free amines are in parenthesis)
Bu^nNH_2	$-C\underline{H}_2NH_2$ 3.34(2.70); $-C\underline{H}_2CH_2NH_2$ 1.61(1.41) $-C\underline{H}_2CH_2NH_2$- 1.33(1.40); $-C\underline{H}_3$ 0.88(0.92)
$Bu^nN^+H_3$	$-C\underline{H}_2NH_2$ 3.0(3.0); $-C\underline{H}_2CH_2NH_2$ 1.74(1.74) $-C\underline{H}_2CH_2NH_2$- 1.45(1.45); $-C\underline{H}_3$ 0.95(0.95)
Pr^nNH_2	$-C\underline{H}_2NH_2$ 3.34(2.66); $CH_3C\underline{H}_2$- 1.54(1.46); $-C\underline{H}_3$ 0.87(0.91)
Pr^iNH_2	$-C\underline{H}CH_3$ 3.41(3.12); $C\underline{H}_3$ 1.19(1.08)
Bu^tNH_2	$-C\underline{H}_2NH_2$ 2.61(2.50); $(CH_3)_2C\underline{H}$- 1.77(1.58); $-C\underline{H}_3$ 0.92(0.89)

The liquid-liquid extraction[20] of alkali metal cations by the transition metal rimmed cavitands, **4** and **5**, has been carried out. The results shown in Table 4 indicate that the whole group of alkali metal cations can be extracted by **4** and **5**. The alkali cation selectivity of those complexes is quite different from other calixresorcinarene derivatives, which normally have strongest affinity for Cs^+.[20] These transition metal rimmed cavitands show more affinity for K^+ than for other alkali metal ions. Attempts to grow crystals of either the amine or alkali metal cation inclusion complexes have not been successful and further speculation about the nature of the binding is probably not justified.

Table 4. Extraction of alkali picrates in CH_2Cl_2 at 25°C by transition metal calixresorcinarene derivatives **4a** and **5**

Ligands	Picrate Salt Extracted(%)					
	Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+
4a	52.6	63.5	70.0	60.8	56.3	58.6
5	45.1	69.7	74.3	47.4	32.8	26.2

Aqueous phase: [Metal Chloride] = 0.1M; [Picric acid] = 8.1×10^{-5}M
Organic phase: [ligand] = 8.1×10^{-5}M; Receptor solution (5mL) was shaken (3min) with picrate solution (5mL) and % extraction was measured from the absorbance at 357nm of the resulting CH_2Cl_2 solution and aqueous solution. No picrate extraction was observed in the absence of ligands.

2.2.5 Preparation of "Octopus" Phosphinito-Calixresorcinarene Derivatives

Calixresorcinarene **1** has a total of eight OH groups around its upper rim. It should also be possible for **1** to react with $ClPPh_2$ to give an open octa-phosphinito macrocyclic ligand. Thus, treatment of **1** with excess of $ClPPh_2$ in the presence of pyridine gave the

desired product 3 with eight phosphinito groups attached to the upper rim of the calixresorcinarene.

The ^{31}P NMR spectrum of 3 shows two singlets of equal intensity at δ=108ppm and 104.4ppm. The observation of two ^{31}P NMR resonances was unexpected and so molecular mechanics calculations were carried out in an attempt to define the stereochemistry of 3. These calculations[9] indicated that the bulky PPh_2 groups force the bowl to adopt a flattened cone conformation in order to minimize steric repulsions between adjacent PPh_2 groups. Several conformers with different orientations of PPh_2 groups have almost equal energy but there is a preference for structures in which alternating PPh_2 groups are directed inwards or outwards with respect to the centre of the flattened bowl. A possible structure is illustrated in Figure 5. Presumably, restricted rotation of the Ph_2PO units due to steric hindrance leads to the observation of two ^{31}P resonances, one for the inward and one for the outward directed PPh_2 groups.

2.2.6 Coordination Chemistry of [Calixresorcinarene$(OPPh_2)_8$], 3

The complexing behaviour of 3 was explored. It is interesting to note that the PPh_2 groups on the upper rim of 3 are fairly close (4.5~5.5Å) and have some flexibility. Hence, unlike the situation for 2, they could act either as monodentate ligands to eight different metal centres or as chelate ligands to four metal centres. When 3 was treated with $AuCl(SMe_2)$ in CH_2Cl_2, it acted as a terminal ligand to give a "gilded octopus molecule", 8, in which each gold(I) centre is 2-coordinate. For this complex, only one ^{31}P resonance

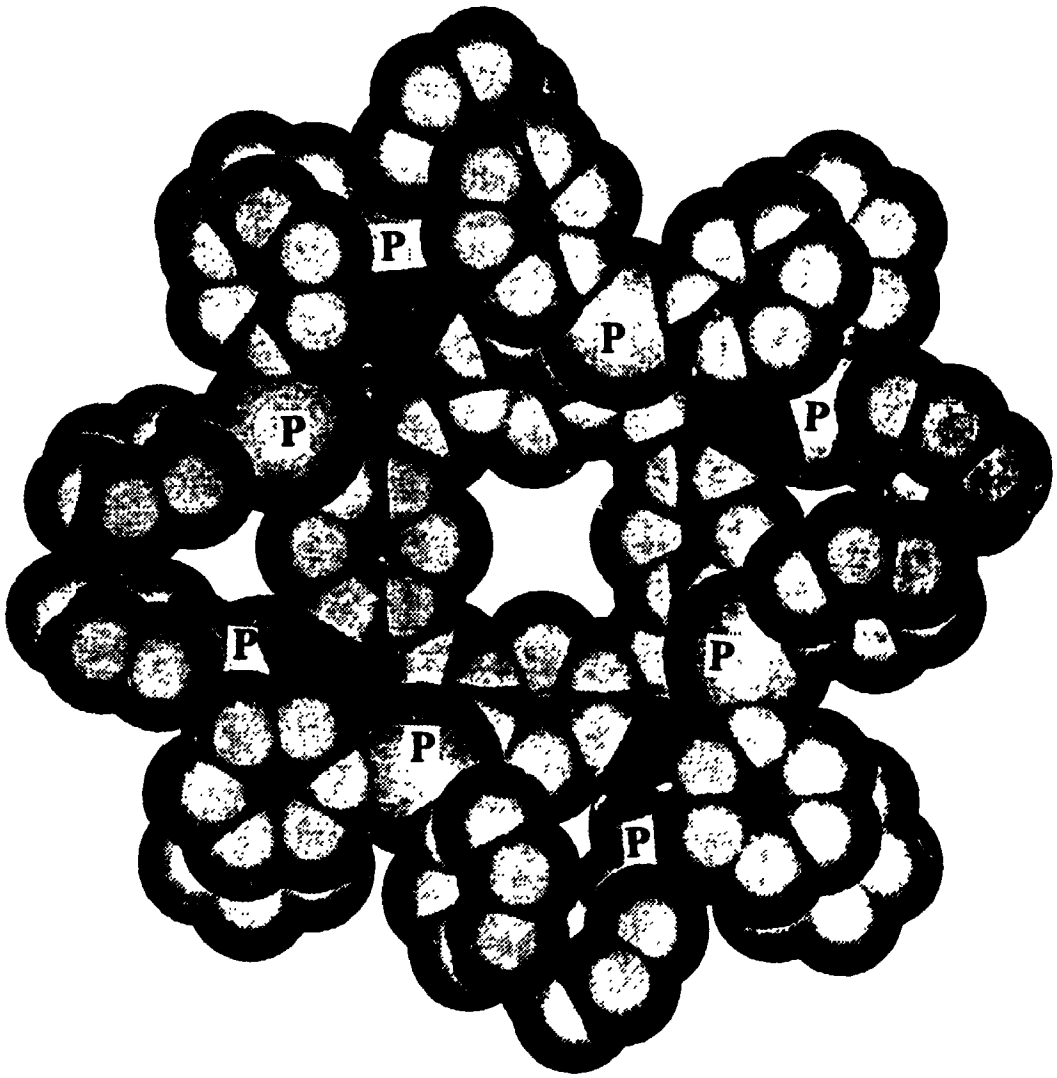
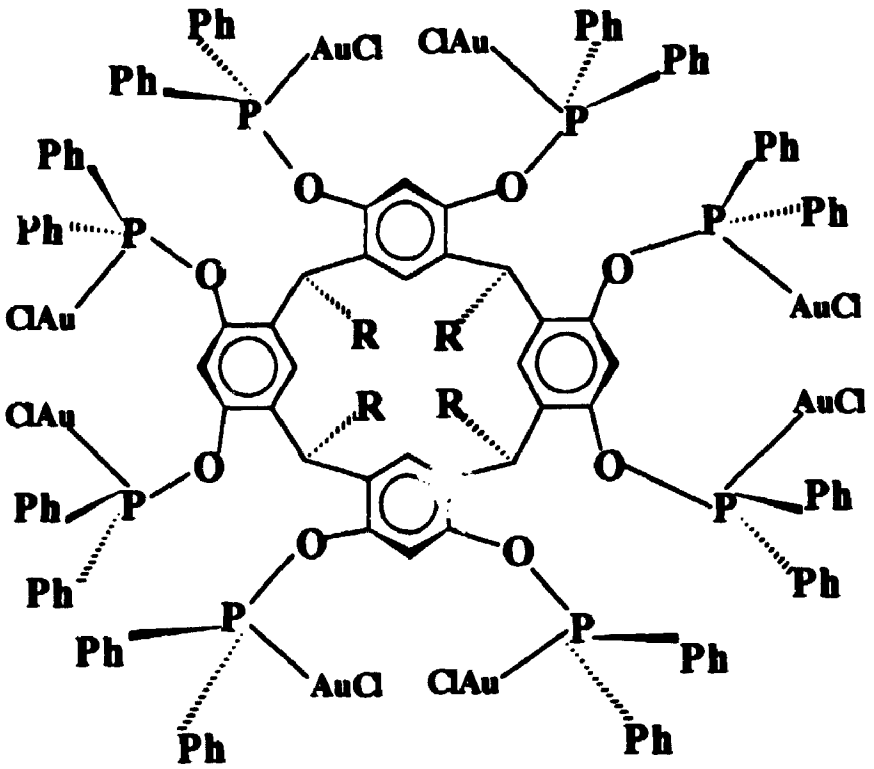


Figure 5. Space filling model of phosphinito-calixresorcinarene 3

was observed showing that it adopts a more symmetrical conformation than the parent ligand. Since addition of AuCl groups will not reduce steric hindrance to rotation of PPh_2 groups, it is proposed that all AuCl group are directed inwards with respect to the flattened bowl. This may allow weak Au...Au bonding between neighbouring AuCl units.



8

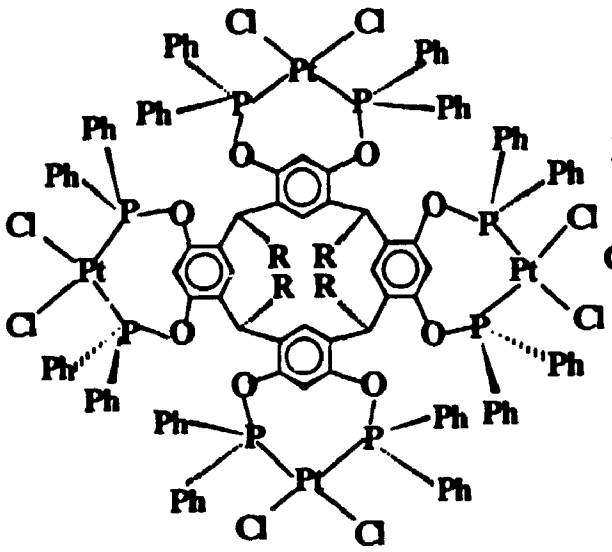
Ligand **3** reacted with $[PtCl_2(SMe_2)_2]$ to gave complexe **9**. There are four possible ways for the ligand to chelate metals as shown in Figure 6, structures G-J. It is possible to have cis- or trans-chelation by pairs of phosphorus atoms attached to the same aryl rings to give eight membered rings (structures G, H) as well as cis- or trans-chelation by phosphorus atoms attached to adjacent aryl rings to give ten membered rings (structures I, J). Molecular mechanics calculations indicated that the product G, involving cis-

chelation by phosphorus atoms on the same aryl ring to give eight membered rings has much lower angle strain and steric hindrance than the other three possibilities. Complex **9** gave a sir glet in the ^{31}P NMR spectrum indicating that all phosphorus atoms are equivalent. The cis-chelation is readily proved by the magnitude of the coupling constant $^{1}J(Pt\text{-}P) = 4431$ Hz, consistent with the a phosphinite trans to chloride but too high for a phosphinite trans to another phosphinite.[10]

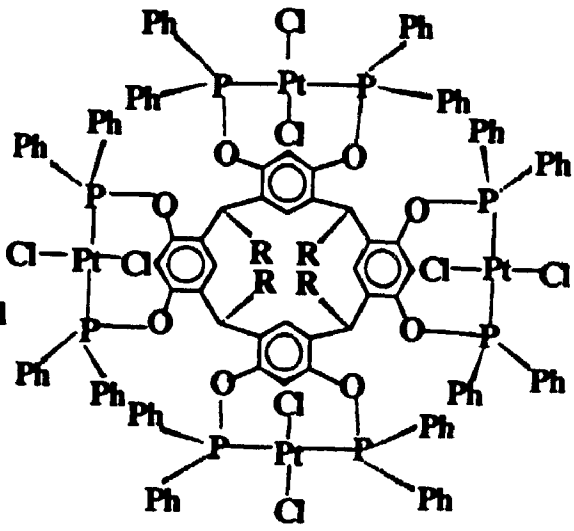
The peaks in the ^{1}H NMR spectra of **8**, **9** are broadened probably because of the equilibration of different conformers and this effect made it difficult to study the inclusion chemistry of these compounds by ^{1}H NMR techniques.

2.3. EXPERIMENTAL SECTION

The complexes $[AuCl(SMe_2)]$,[21] $[PtCl_2(SMe_2)_2]$,[22] and the calixresorcinarene **1**[5] were prepared by literature methods. All the experim. nts were carried out by using standard Schlenk techniques. NMR spectra were recorded by using a Varian Gemini 300MHz spectrometer. ^{1}H NMR chemical shifts were measured relative to deuterated solvent peaks, but were reported relative to tetramethylsilane. ^{31}P NMR chemical shifts were determined relative to 85% H_3PO_4 as external standard. IR spectra were recorded on a Bruker IFS32 FTIR spectrometer with Nujol mulls. Elemental analyses were perfo.med by Galbraith Laboratories Inc., Knoxville, TN, USA. Mass spectra were recorded on a FINNEGAN MAT 8230 mass spectrometer.



Structure G



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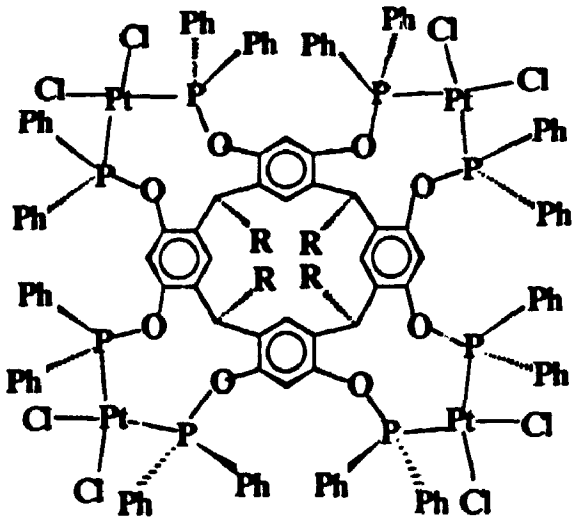
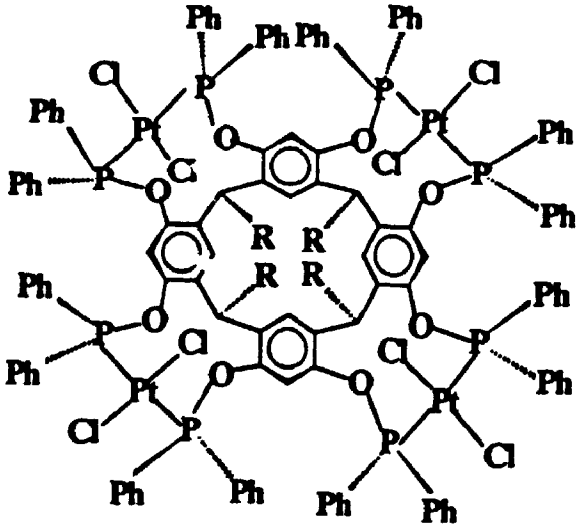


Structure I



Structure J

Figure 6. Structures of four possible isomers of compound 9

2.3.1 Calixresorcinarene[O_2PPh]$_4$, 2

A suspension of 1 (1.81g, 2mmol) in a mixture of dry ether (100mL) and pyridine (2.5mL) was cooled to -40°C and then phenylphosphonous chloride (1.1mL, 8.1mmol) was added slowly. The mixture was stirred for 4h then allowed to warm to room temperature. The mixture was stirred for another 24h and then hexane (50mL) was added to the mixture. The white precipitate was collected by filtration, washed with hexane (3×20mL) and dried under vacuum. The solid was then washed with water (2×200mL) and dried under vacuum immediately. Compound 2 (2.15g), which was mixed with small amount of pyridinium chloride impurity, is suitable for further reactions. Small amounts of pure sample can be obtained by column chromatography with Et_2O/hexane (1:1) as eluent. Typical spectroscopic data 2: NMR in CD_2Cl_2: $\delta(^{31}P)$ = 166.3 [s]. $\delta(^1H)$ = 2.68 [br, s, 16H, $C\underline{H}_2C\underline{H}_2Ph$], 4.86 [br, dt, 4H, $C\underline{H}(CH_2)_2Ph$], 6.75 [t, 4H, Ar$\underline{H}$, ortho to O], 7.09-7.30 [m, 20H, $C_6\underline{H}_5$], 7.41 [s, 4H, Ar$\underline{H}$, meta to O], 7.48-7.58 [m, 12H, $PC_6\underline{H}_5$, para and meta to P], 7.80-7.79 [m, 8H, $PC_6\underline{H}_5$, ortho to P]. EI-MS: m/e = 1328.394; calc. for $C_{84}H_{68}O_8P_4$ 1328.386.

2.3.2 Calixresorcinarene[$OPPh_2$]$_8$, 3

Calixresorcinarene 1 (1.81g, 2mmol) was suspended in a solution of ethyl ether (100mL) with pyridine (5mL). The solution was cooled at -78°C and diphenylphosphinous chloride (3.1mL, 16mmol) was slowly added. The mixture was stirred at -78°C for 2h, then it was allowed to warm to room temperature and stirred for another 36h. Hexane (50mL) was

added to the mixture. The solid was filtered off and washed twice with hexane. The product was extracted from the solid by benzene (50mL). The benzene was evaporated and 3 was obtained as white solid. Yield: 2.1g, 44.2%. Anal. Calc for 3, $C_{156}H_{128}O_8P_8$: C, 78.8; H, 5.4; P, 10.4. Found: C, 78.4; H, 5.9, P, 10.7%. NMR in C_6D_6: $\delta(^{31}P)$ = 108.0 [s] and 104.4ppm [s] in 1:1 intensity ratio. $\delta(^1H)$ = 2.3-2.7 [br, 16H, $C\underline{H}_2C\underline{H}_2Ph$], 4.3 [br, 4H, $C\underline{H}(CH_2)_2Ph$], 6.7-7.8 [m, 108H, Ar$\underline{H}$]. IR: ν_{OH} absent.

2.3.3 Calixresorcinarene$[O_2PPh.AuCl]_4$, 4

A mixture of $AuCl(SMe_2)$ (0.20g, 0.68mmol), and 2 (0.23g, 0.17mmol) in CH_2Cl_2 (20mL) was stirred at room temperature for 2h. The CH_2Cl_2 and SMe_2 were removed completely under vacuum. The residue was redissolved in CH_2Cl_2 and crystallized by diffusion with MeCN. A light yellow solid was obtained, which was washed with MeCN and dried under vacuum. Yield: 0.32g, 82%. Anal. Calc. for 4 $C_{84}H_{68}Au_4Cl_4O_8P_4$: C, 44.7; H, 3.0; Cl 6.3. Found C, 45.0; H, 2.8; Cl, 6.2%. NMR in $CDCl_3$: $\delta(^{31}P)$ = 144 [s]; $\delta(^1H)$ = 2.70-2.82[m, br, 16H, $C\underline{H}_2C\underline{H}_2Ph$], 4.74 [br, 4H, $C\underline{H}(CH_2)_2Ph$], 6.93[t, $^4J(PH)$ = 1.8 Hz, 4H, Ar$\underline{H}$, ortho to O), 7.15-7.21[m, 8H, $C_6\underline{H}_5$], 7.26-7.35[m, 12H, $C_6\underline{H}_5$], 7.51[s, 4H, Ar$\underline{H}$, meta to O], 7.49-7.65[m, 12H, $PC_6\underline{H}_5$, para and meta to P], 7.98-8.10[m, 8H, $PC_6\underline{H}_5$, ortho to P]. FAB-MS: m/e = 2026; calc.for M^+-(AuCl) 2026.

2.3.4 Crystal Structure Data of 4

Formula: $C_{84}H_{68}Au_4Cl_4O_8P_4.2.5CH_3CN.0.5CH_2Cl_2.H_2O$, M = 2422.16, T = 298 K,

Triclinic, space group $P\bar{1}$, a = 15.271(5), b = 28.399(8), c = 11.060(5) Å, α = 93.40(3), β = 111.21(3), γ = 98.41(2)°, V = 4390.8(5) Å^3, Z = 2, D_{obs} = 1.87(5) g cm^{-3}, D_{calc} = 1.83 g cm^{-3}, R = 0.0534, R_w = 0.0504. The crystal structures were solved by Dr. J. J. Vittal Data were obtained by using an Enraf Nonius CAD4F diffractometer with graphite monochromator and MoKα radiation at λ = 0.71073 Å wavelength.

2.3.5 Calixresorcinarene[O_2PPh.$PtCl_2SMe_2$]$_4$, 5:

A mixture of $PtCl_2(SMe_2)_2$ (0.193g, 0.495mmol) and 3 (0.165g, 0.124mmol) in CH_2Cl_2 (20mL) was stirred at room temperature for 2h. The CH_2Cl_2 and SMe_2 were removed completely under vacuum. The residue was redissolved in CH_2Cl_2 and crystallized by diffusion with MeCN. A yellow solid was obtained which was washed with MeCN and dried under vacuum. Yield: 0.141g, 43%. Anal. Calc. for $C_{92}H_{92}Cl_8O_8P_8Pt_4S_4$ 5: C 41.8, H 3.5; Found:C 41.4; H 3.5%. NMR in $CDCl_3$: $\delta(^{31}P)$ = 87.7 [s, $^1J_{P\text{-}Pt}$ = 4965Hz]; $\delta(^{195}Pt)$ = -2325 [d, $^1J_{P\text{-}Pt}$ = 4966Hz]; $\delta(^1H)$ = 2.72 [s, $^3J_{H\text{-}Pt}$ = 52Hz, SMe_2], 2.8-2.6[m, br, 16H, $C\underline{H}_2C\underline{H}_2Ph$], 4.65 [t, 4H, $^3J_{H\text{-}H}$ = 7Hz, $C\underline{H}(CH_2)_2Ph$], 7.84[t, $^4J_{PH}$ = 2Hz, 4H, Ar$\underline{H}$, ortho to O], 7.0-7.2[m, 20H, $C_6\underline{H}_5$], 7.17[s, 4H, Ar$\underline{H}$, meta to O], 7.4-7.6[m, 12H, $PC_6\underline{H}_5$, para and meta to P], 8.04 [m, 8H, $PC_6\underline{H}_5$, ortho to P].

2.3.6 Calixresorcinarene[O_2PPh.Rh(CO)(μ-Cl)]$_4$, 6

A mixture of $[Rh(CO)_2Cl]_2$ (0.33g, 0.33mmol) and 2 (0.20g, 0.15mmol) in CH_2Cl_2 (20mL) was stirred at room temperature for 3h to give a yellowish solution Some

CH_2Cl_2 (ca. 15mL) was removed under vacuum and then MeCN was diffused into the solution. A light yellow solid was obtained, which was washed with MeCN and dried under vacuum. Yield: 0.27g, 88%. Anal. Calc. for 6 $C_{88}H_{68}Cl_4O_{12}P_4Rh_4$: C, 53.0 H, 3.4. Found C, 52.8; H, 3.1%. NMR in $CDCl_3$: $\delta(^{31}P)$ = 143.4 [d ^1J(Rh-P)=236.5Hz]; $\delta(^1H)$ = 2.60-2.68[br, 16H, CH_2CH_2Ph], 4.68 [br, 4H, $CH(CH_2)_2Ph$], 7.09-8.03 [m, 48H, ArH]. IR: ν_{CO} = 2009cm^{-1} (s).

2.3.7 Calixresorcinarene[$O_2PPh.Ir(\eta^2$-COD)(μ-Cl)]$_4$, 7

A mixture of $[Ir(COD)Cl]_2$ (0.21g, 0.31mmol) and 2 (0.20g, 0.15mmol) in CH_2Cl_2 (20mL) was stirred at room temperature for 3h to give a yellow solution. Partial CH_2Cl_2 (15mL) was removed under vacuum and then MeCN was diffused into the solution. A yellow solid was obtained, which was washed with MeCN and dried under vacuum. Yield: 0.29g, 71.2%. Anal. Calc. for 7: $C_{116}H_{116}Cl_4Ir_4O_8P_4.CH_2Cl_2$: C, 50.9; H, 4.6, Found C, 50.5; H, 4.3%. NMR in $CDCl_3$: $\delta(^{31}P)$ = 122.7 [s]; $\delta(^1H)$ = 2.27-2.40 [br, 16H, CH_2CH_2Ph], 5.30 [s, 2H, CH_2Cl_2], 4.38 [br, 4H, $CH(CH_2)_2Ph$], 6.90[4H, ArH, ortho to O], 7.00-7.90[m, br, 44H, Ar-H]. 5.50[br, 8H, (COD)=CH], 3.20[br, 8H, (COD)=CH...Ir], 1.8-2.2(m, br, 32H, COD]. IR: $\nu_{C=C}$ = 1653cm^{-1} (s)

2.3.8 Calixresorcinarene($OPPh_2AuCl)_8$, 8

A mixture of $AuCl(SMe_2)$ (0.20g, 0.68mmol) and calixresorcinarene($OPPh_2$)$_8$ 3 (0.20g, 0.084mmol) in CH_2Cl_2 (20mL) was stirred at room temperature for 15h. The CH_2Cl_2 and

SMe_2 were removed completely under vacuum. The residue was redissolved in CH_2Cl_2 and crystallized by diffusion with toluene. A white solid was obtained and was washed with benzene and dried under vacuum. Yield: 0.27g, 76%. Anal. Calc for **8**, $C_{156}H_{128}Au_8Cl_8O_8P_8$: C, 44.2; H, 3.1; P, 5.9; Found: C, 44.2; H, 3.0; P, 5.9%. NMR in $CDCl_3$: $\delta(^{31}P)$ = 87.5 [s]. $\delta(^1H)$ = 2.68[br, 16H, $C\underline{H}_2C\underline{H}_2Ph$], 4.45 [br, 4H, $\underline{H}(C\underline{H}_2)_2Ph$], 6.3[br, 4H, Ar$\underline{H}$, ortho to O], 7.2-7.88[m, 104H, Ar$\underline{H}$]

2.3.9 Calixresorcinarene-$(OPPh_2)_8(\mu\text{-}PtCl_2)_4$, **9**

A mixture of $PtCl_2(SMe_2)_2$ (0.13g, 0.34mmol) and **3** (0.20g, 0.084mmol) in CH_2Cl_2 (20mL) was stirred at room temperature for 15h. The CH_2Cl_2 and SMe_2 were removed completely under vacuum. The residue was redissolved in CH_2Cl_2 and crystallized by diffusion with benzene. A white solid was obtained, which was washed with benzene and dried under vacuum. Yield: 0.22g, 76.2%. Anal. Calc. for **9**, $C_{156}H_{128}Cl_8O_8P_8Pt_4$: C, 54.5; H, 3.8; P, 7.2. Found: C, 54.2; H, 3.7; P, 7.1%. NMR in $CDCl_3$: $\delta(^{31}P)$ = 84.9 [s, ^1J(Pt-P) = 4431Hz]. $\delta(^1H)$ = 2.54[br, 16H, $C\underline{H}_2C\underline{H}_2Ph$], 4.4-4.5[br, 4H, $C\underline{H}(C\underline{H}_2)_2Ph$], 6.7-8.0[m, 108H, Ar$\underline{H}$].

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Chapter Three

A NOVEL ANION RECEPTOR MODEL SYSTEM

3.1 INTRODUCTION

Virtually all of the known macrocyclic compounds of host-guest chemistry are polybasic hosts such as polyethers, amines, sulphides and carbonyl compounds and they interact with neutral or positively charged guests such as toluene, acetone, chloroform, metal cations and ammonium salts. It is quite surprising to note that, compared to cation complexation, anion complexation has received very little attention, although anion complexation plays important roles in organic, inorganic and biological chemistry.[1] The study of anion inclusion has implications for a number of areas in chemistry and biochemistry. In biology, it was reported that anionic substrates participated in approximately 70% of all enzymatic reactions.[2] Anions are necessary partners of all positive centers. Their functions are of the same importance as those of cations.[2] In chemistry, anions play many roles as nucleophiles, bases, redox agents, in phase-transfer catalysis and others. Inclusion of anions can bring changes in chemical reactivity of the anions as does cation complexation. Furthermore, once anions are captured, the 'naked cation' chemistry will be another interesting area to explore.

The first model system for anion inclusion was conceptually derived from the class of cation complexing agents known as aza crown ethers.[3,4] When polyprotonated, these macrocyclic polyamines form cavities lined with positive charges. The distance between

charged sites, the cavity size and the potential for hydrogen bonding all play a role in determining the affinity of an anion for a particular host. A second approach to anion fixation is by the polycyclic quaternary ammonium salts. Anion inclusion by these model systems was dominated by direct electrostatic interactions and hydrogen bonding as illustrated in Figure 1.[5,6] In such anion receptor model systems, the anion could form either an endo complex with full cavity incorporation or, more often, it can bind outside the cavity and the ionic and nucleophilic properties of the captured anions are then changed only slightly.[7,8]

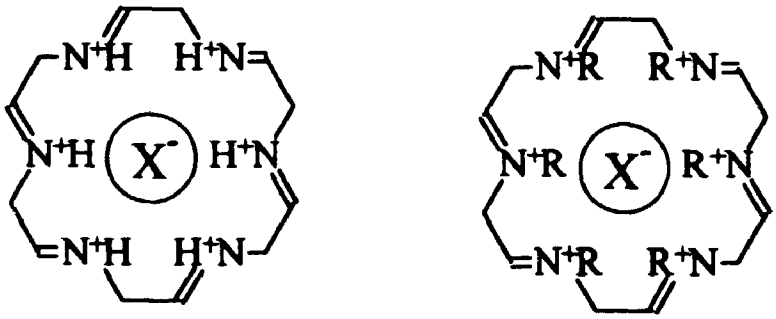
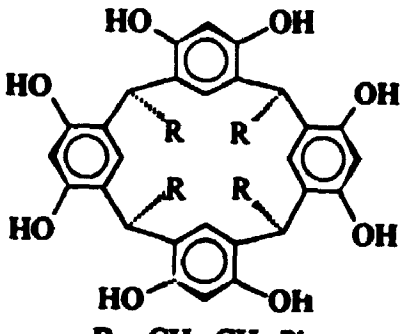


Figure 1. Polycyclic ammonium anion receptor models

It is well known that a rim of nucleophilic atoms such as oxygen, nitrogen and sulfur in crown ethers or cryptands can include a variety of cations. Whether a rim of electron-deficient transition metals incorporated into a macrocyclic framework can create a suitable environment to include an anion by multiple coordination is an interesting question.

The first macrocyclic system we chose to explore was based on the calixresorcinarenes 1. Calixresorcinarenes are bowl shaped molecules with a remarkable ability to contain either neutral or cationic guests.[9-11] However, owing to the poor electrophilicity of

calixresorcinarenes, there is little anion inclusion chemistry and no halide inclusion [12]. Most known metal derivatives of calixarenes are with oxophilic metal ions, which cannot easily be used for anion inclusion. Therefore, in these complexes, inclusion of neutral molecules is still preferred.[13-16] The special coordination properties of the phosphonito-calixresorcinarene 2, which has been discussed in chapter 2, are notable and it forms the two coordinate AuCl-derivative 3, in which there is a "metal picket fence" around the upper rim of the bowl with one AuCl unit tilting to the centre of the bowl. Although the gold(I) rimmed calixresorcinarene 3 derivative did not show anion inclusion properties, it demonstrated the possibility for anion inclusion if more electron-deficient metal centers than gold(I) could be introduced. In this chapter, the successful introduction of copper(I) and silver(I) centres around the upper rim of a calixresorcinarene and the unique anion inclusion properties of these compounds will be reported.



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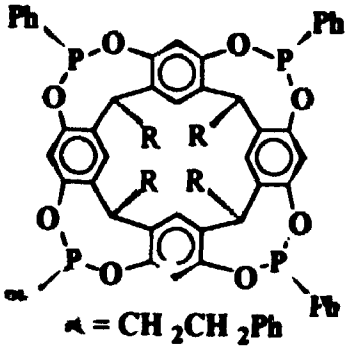

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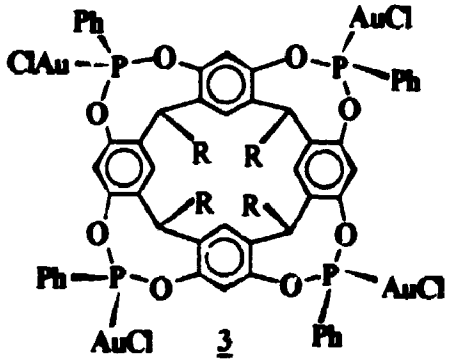


3

3.2 RESULTS AND DISCUSSIONS

3.2.1 Synthesis of Copper(I) Rimmed Calixresorcinarenes

The phosphorus(III) derivative **2** of a calixresorcinarene, in which the lone pair electrons on the phosphorus atoms are directed inwards, can be obtained from reaction of the calix[4]resorcinarene **1** and $PPhCl_2$ with pyridine as base, as described in chapter 2. Treatment of the ligand **2** with $(CuCCPh)_n$ in the presence of pyridinium chloride, gave $[C_5H_5NH]^+[LCu_4(\mu\text{-}Cl)_4(\mu_3\text{-}Cl)]^-$, **4a** in high yield (76%) with release of HCCPh which could be recovered quantitatively. Ligand **2** failed to react with $(CuCCPh)_n$ in the absence of pyridinium chloride. The single resonance observed in the ^{31}P NMR spectrum of complex **4a** in CD_2Cl_2 suggested that the complex has C_4 symmetry in solution. The ^1H NMR spectrum of complex **4a** also clearly indicated that the complex **4a** still has the cone conformation. It was interesting to note that the ^1H NMR spectrum of **4a** showed that a pyridinium cation co-existed with the copper(I) product. Did that indicate anion inclusion? The anion occluded structure of **4a** was finally confirmed by X-ray structure determination and the structure of the complex anion is shown in Figure 2. The main structural features are summarized as follows:

1) There is a $Cu_4(\mu\text{-}Cl)_4$ unit arranged in a crown shape around the bowl rim, thus closing the bowl, in which the Cu-Cl bond distances are in the range 2.306(6)-2.410(5) Å which is normal for Cu-Cl bonds.[17]

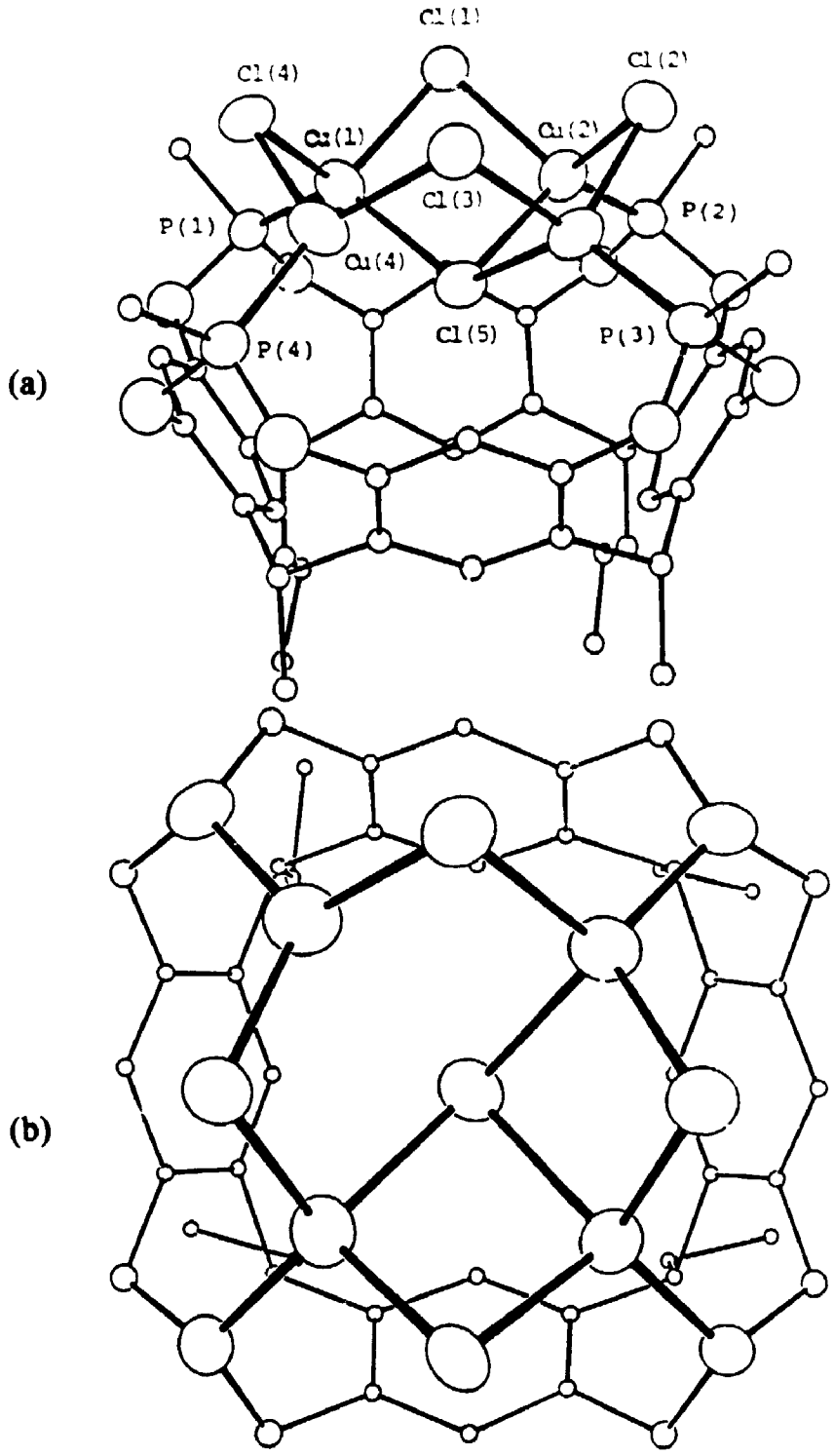


Figure 2. a) A side view of the molecular structure of **4a**;

b) A front view of the molecular structure of **4a**

The phenyl rings on both PhP and -CH_2CH_2Ph groups and hydrogens have been omitted for clarity

2) A Cl^- ion is trapped inside the bowl and is more weakly bound to three of the copper atoms with Cu-Cl distances in the range 2.467(5)-2 548(6) Å. These distances are longer than the other Cu-Cl distances apparently indicating a weaker Cu-Cl bonding. The distances Cu(4)-Cl(5) is 2.983(5)Å which is considered too long for a Cu-Cl bond.[17]

3) As a result, the atoms Cu(1)-Cu(3) have irregular tetrahedral geometries with bond angles Cl-Cu-Cl in the range 95.1(2)-109.7(2)° while Cu(4) has trigonal planar geometry. The crown structure observed in **4a** is rare in tetranuclear copper(I) halide derivatives, for which cubane or ladder structures are typical.[18] The counterpart of the anion, namely the pyridinium cation was found to be disordered around the upper rim. The disorder was resolved with two models having multiplicities 0.70 and 0.30. For this reason, the nitrogen atom could not be distinguished from the carbon atoms in each model and hence a disorder of the N atom over all six sites was assumed. The bond distances and angles are listed in Table 1.

As mentioned before, the ^{31}P NMR spectrum of complex **4a** in CD_2Cl_2 solution contains only one resonance either at room temperature or -90°C whereas, in the solid state, according to the crystal structure, three such resonances would be expected. This indicates that the anion **4a** is fluxional in solution, with the trapped μ_3-Cl^- migrating rapidly between the four copper atoms to give effective four-fold symmetry. This type of anion inclusion demonstrated by compound **4a** appears to be unique in both calixarene chemistry and supramolecular chemistry and is made possible by the presence of the electrophilic copper(I) centres.

Table 1. Selected bond distances (Å) and angles (°) of **4a**

(a) Selected bond distances (Å)

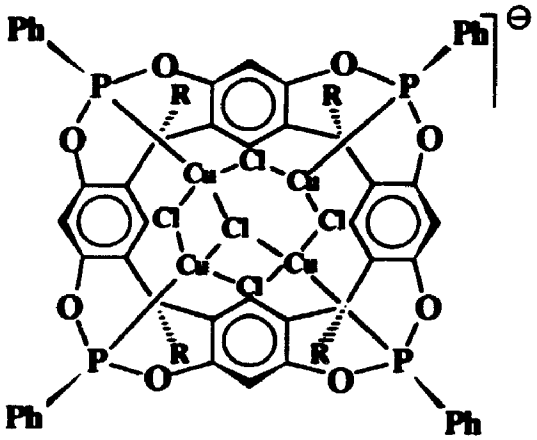
Cu(1)-Cl(1) 2.374(5)	Cu(1)-Cl(4) 2.405(5)	Cu(1)-Cl(5) 2.512(5)
Cu(2)-Cl(1) 2.348(5)	Cu(2)-Cl(2) 2.386(5)	Cu(2)-Cl(5) 2.548(6)
Cu(3)-Cl(2) 2.410(5)	Cu(3)-Cl(3) 2.369(5)	Cu(3)-Cl(5) 2.467(5)
Cu(4)-Cl(3) 2.294(6)	Cu(4)-Cl(4) 2.306(6)	Cu(1)-P(1) 2.177(6)
Cu(2)-P(2) 2.177(5)	Cu(3)-P(3) 2.181(5)	Cu(4)-P(4) 2.168(6)
P(1)-O(1) 1.633(12)	P(1)-O(2) 1.632(12)	P(2)-O(3) 1.627(11)
P(2)-O(4) 1.641(11)	P(3)-O(5) 1.636(12)	P(3)-O(6) 1.631(12)
P(4)-O(7) 1.610(13)	P(4)-O(8) 1.638(13)	P(1)-C(111) 1.771(15)
P(2)-C(211) 1.787(14)	P(3)-C(311) 1.770(16)	P(4)-C(411) 1.767(17)

(b) Selected bond angles (°)

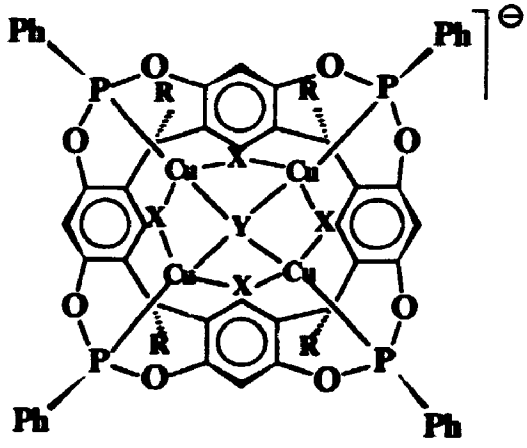
Cl(4)-Cu(1)-Cl(1)	107.5(2)	Cl(5)-Cu(1)-Cl(1)	95.4(2)
Cl(5)-Cu(1)-Cl(4)	100.6(2)	P(1)-Cu(1)-Cl(1)	114.7(2)
P(1) -Cu(1)-Cl(4)	109.7(2)	P(1)-Cu(1)-Cl(5)	126.7(2)
Cl(2)-Cu(2)-Cl(1)	105.5(2)	Cl(5)-Cu(2)-Cl(1)	95.1(2)
Cl(5)-Cu(2)-Cl(2)	95.1(2)	P(2)-Cu(2)-Cl(1)	117.6(2)
P(2) -Cu(2)-Cl(2)	114.0(2)	P(2)-Cu(2)-Cl(5)	125.6(2)
Cl(3)-Cu(3)-Cl(2)	106.6(2)	Cl(5)-Cu(3)-Cl(2)	96.7(2)
Cl(5)-Cu(3)-Cl(3)	96.9(2)	P(3)-Cu(3)-Cl(2)	110.7(2)
P(3) -Cu(3)-Cl(3)	114.0(2)	P(3)-Cu(3)-Cl(5)	129.2(2)
Cl(4)-Cu(4)-Cl(3)	110.0(2)	P(4)-Cu(4)-Cl(3)	121.1(2)
P(4) -Cu(4)-Cl(4)	120.3(2)	Cu(2)-Cl(1)-Cu(1)	86.4(2)
Cu(3)-Cl(2)-Cu(2)	85.5(2)	Cu(4)-Cl(3)-Cu(3)	95.8(2)
Cu(4)-Cl(4)-Cu(1)	91.7(2)	Cu(2)-Cl(5)-Cu(1)	79.4(2)
Cu(3)-Cl(5)-Cu(1)	126.9(2)	Cu(3)-Cl(5)-Cu(2)	81.0(2)
O(1)-P(1)-Cu(1)	117.6(5)	O(2)-P(1)-Cu(1)	118.5(5)
O(2)-P(1)-O(1)	102.0(6)	C(111)-P(1)-Cu(1)	116.9(5)
C(111)-P(1)-O(1)	98.4(6)	C(111)-P(1)-O(2)	100.1(6)
O(3)-P(2)-Cu(2)	118.4(4)	O(4)-P(2)-Cu(2)	117.1(4)
O(4)-P(2)-O(3)	101.1(6)	C(211)-P(2)-Cu(2)	118.5(4)
C(211)-P(2)-O(3)	98.3(6)	C(211)-P(2)-O(4)	100.0(6)
O(5)-P(3) -Cu(3)	116.6(5)	O(6)-P(3)-Cu(3)	117.1(5)
O(6)-P(3) -O(5)	100.7(6)	C(311)-P(3)-Cu(3)	118.4(5)
C(311)-P(3) -O(5)	101.2(6)	C(311)-P(3)-O(6)	99.8(6)
O(7)-P(4) -Cu(4)	118.6(5)	O(8)-P(4)-Cu(4)	117.2(5)
O(8)-P(4) -O(7)	102.4(7)	C(411)-P(4)-Cu(4)	118.8(5)

The other halide derivatives of **4** (**4b**, X=Br; **4c**, X=I) can be obtained either from **3a** by halide exchange using LiBr and NaI respectively or by direct reaction of ligand **2** with $(CuCCPh)_n$ in the presence of $C_5H_5N.HCl$ and LiBr or NaI. The occluded μ_3-Cl as well as the more exposed μ_2-Cl ligands of **4a** are readily replaced by bromide or iodide. Other anions such as BF_4^- and PF_6^- cannot be trapped inside. The closed cavity formed by ligand **2** and the Cu_4Cl_4 aggregate is probably too small to accommodate the larger anions and the difficulty of these anions to act as μ_3 face-bridging ligands may also limit their ability to be included.

The difference in the preferred stereochemistries of gold(I) and copper(I) clearly has a profound effect on the ability of the bowl complexes to occlude a halide ion. The gold complex does not bind halide ions strongly whereas the copper complex does. Clearly, by modifying the metal substituents, there is the potential to tune the halide binding ability.



4a



4b (Y = X = Br); **4c** (Y = X = I)
4d and **4e** (Y = I, X = $Cl_{1.75}I_{2.25}$)

3.2.2 Anion Recognition by Copper(I) Rimmed Calixresorcinarenes

As mentioned before, selective anion inclusion is very important in both biochemistry and chemistry. Can anions be included **selectively** in **4**? In attempts to prepare the iodide analogue of **4a**, reactions between **2** and CuI in the presence of pyridinium chloride or between **4a** and n-Bu_4NI were carried out. In each case, the product analyzed as $[C_5H_5NH]^+[\mathbf{2}.Cu_4I_{3.3}Cl_{1.7}]^-$, **4d**, showing that complete replacement of chloride by iodide is difficult. This was unexpected since copper(I) is a soft metal ion with a strong preference for iodide. In this case, we are interested to discover which anion, Cl^- or I^-, has priority to be captured inside the bowl. The ^{31}P NMR spectrum of **4d** showed three broad peaks and its ^1H NMR spectrum indicated the presence of the pyridinium cation. These observations suggested that **4d** has a similar anion inclusion structure as **4a**. Spectroscopic studies of the structure were inconclusive in determining which anion is the guest, but an X-ray structure determination (Figure 3) reveals that the I^- is selectively included in the middle of the bowl by weakly bonding to four Cu atoms, while chloride and iodide ions in a ratio of 1.75:2.25 occupy the μ_2-bridging sites in a disordered way

The occupancy factors for the halogen atoms were obtained from peak heights in the SHELXS-86 solution and later refined in the least-squares refinements Refinement of occupancy factors gave the following ratios I/Cl: X(1) and X(2), 0.625/0.375; X(3), 0.40/0.60; X(4), 0.60/0.40 giving the overall partial formula $[Cu_4I_{3.25}Cl_{1.75}]$, in good agreement with analytical data. The Cu-I(5) distances are 2 752(2)-2 845(2) Å, which are longer than that of normal Cu-I bond (~2.5Å),[17] and adjacent non-bonding Cu. Cu distances

are 3.275-3.461 Å The bond distances and angles are listed in Table 2.

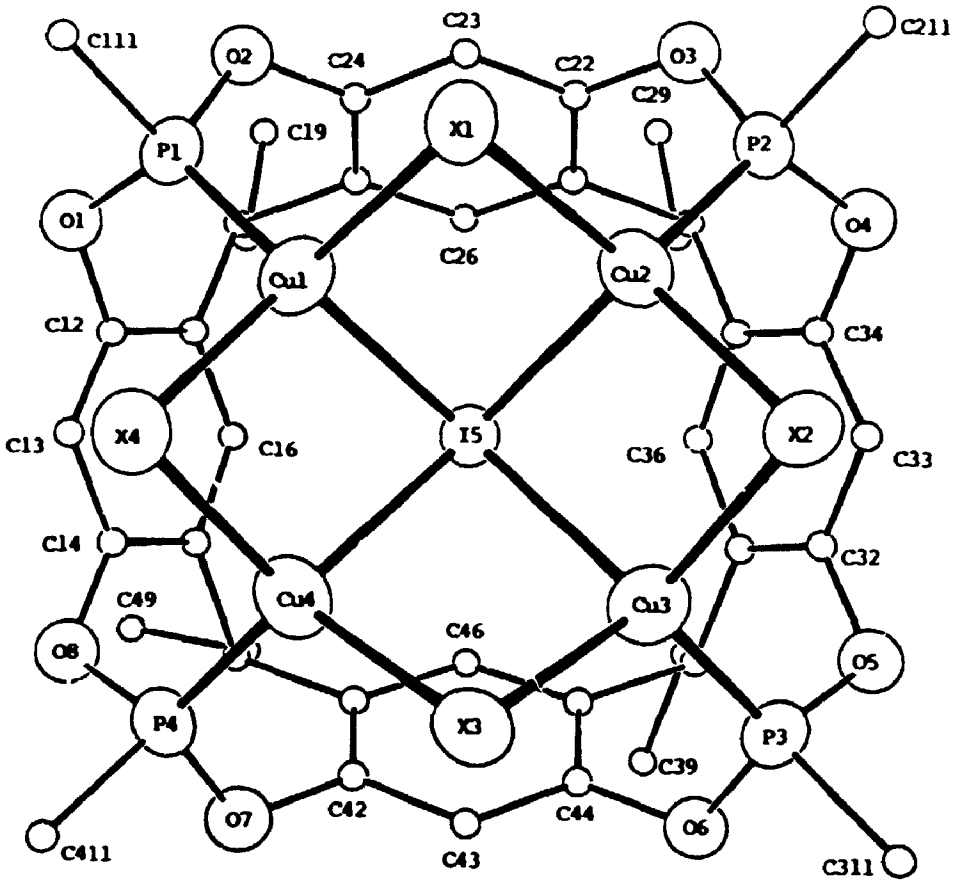


Figure 3. A front view of the molecular structure of **4d**

The phenyl rings on both PhP- and -CH_2CH_2Ph groups have been omitted for clarity.

Table 2. Selected bond distances (Å) and angles (°) of **4d**

(a) Selected bond distances (Å)

Cu(1) - X(1)	2.6300(20)	Cu(2) - X(1)	2.6493(19)
Cu(2) - X(2)	2.6730(20)	Cu(3) - X(2)	2.6453(20)
Cu(3) - X(3)	2.5195(22)	Cu(4) - X(3)	2.5598(23)
Cu(1) - X(4)	2.6642(21)	Cu(4) - X(4)	2.6311(21)
Cu(1) - I(5)	2.7580(18)	Cu(2) - I(5)	2.7520(18)
Cu(3) - I(5)	2.8448(19)	Cu(4) - I(5)	2.8126(18)
Cu(1) - P(1)	2.215(3)	Cu(2) - P(2)	2.216(3)
Cu(3) - P(3)	2.209(3)	Cu(4) - P(4)	2.206(3)
P(1) - O(1)	1.623(8)	P(1) - O(2)	1.646(8)
P(2) - O(3)	1.643(8)	P(2) - O(4)	1.648(8)
P(3) - O(5)	1.638(8)	P(3) - O(6)	1.648(8)
P(4) - O(7)	1.639(8)	P(4) - O(8)	1.645(8)

(b) Selected Bond Angles (°)

X(4)- Cu(1) -X(1)	108.07(7)	I(5)-Cu(1)-X(1)	103.33(6)
I(5)- Cu(1) -X(4)	105.89(6)	P(1)-Cu(1)-X(1)	109.60(11)
P(1)-Cu(1)-X(4)	109.64(11)	P(1)-Cu(1)-I(5)	119.68(10)
X(2)-Cu(2)-X(1)	107.50(6)	I(5)-Cu(2)-X(1)	102.98(6)
I(5)-Cu(2)-X(2)	103.76(6)	P(2)-Cu(2)-X(1)	112.55(11)
P(2)-Cu(2)-X(2)	109.50(11)	P(2)-Cu(2)-I(5)	119.62(10)
X(3)-Cu(3)-X(2)	107.20(7)	I(5)-Cu(3)-X(2)	101.99(6)
I(5)-Cu(3)-X(3)	98.75(7)	P(3)-Cu(3)-X(2)	113.05(11)
P(3)-Cu(3)-X(3)	115.94(11)	P(3)-Cu(3)-I(5)	118.04(10)
X(4)-Cu(4)-X(3)	108.61(7)	I(5)-Cu(4)-X(3)	98.62(7)
I(5)-Cu(4)-X(4)	105.26(7)	P(4)-Cu(4)-X(3)	115.14(12)
P(4)-Cu(4)-X(4)	109.26(11)	P(4)-Cu(4)-I(5)	118.98(10)
Cu(2)-X(1)-Cu(1)	78.33(6)	Cu(3)-X(2)-Cu(2)	79.19(6)
Cu(4)-X(3)-Cu(3)	85.90(7)	Cu(4)-X(4)-Cu(1)	76.41(6)
Cu(2)-I(5)-Cu(1)	74.48(5)	Cu(3)-I(5)-Cu(1)	117.03(5)
Cu(3)-I(5)-Cu(2)	74.53(5)	Cu(4)-I(5)-Cu(1)	72.02(5)
Cu(4)-I(5)-Cu(2)	116.75(5)	Cu(4)-I(5)-Cu(3)	75.43(5)
O(1)-P(1)-Cu(1)	117.0(3)	O(2)-P(1)-Cu(1)	119.1(3)
C(111)-P(1)-Cu(1)	116.3(3)	O(3)-P(2)-Cu(2)	118.0(3)
O(4)-P(2)-Cu(2)	117.0(3)	C(211)-P(2)-Cu(2)	119.2(3)
O(5)-P(3)-Cu(3)	116.7(3)	O(6)-P(3)-Cu(3)	117.6(3)
C(311)-P(3)-Cu(3)	121.2(3)	C(7)-P(4)-Cu(4)	116.7(3)
O(8)-P(4)-Cu(4)	117.9(3)	C(411)-P(4)-Cu(4)	119.6(3)

The positions X(1) and X(2) are occupied by I and Cl atoms in the ratio 0.625:0.375, X(3), 0.40:0.60 and X(4), 0.60:0.40

The complexes $[C_5H_5NH]^+[LCu_4C\ell_5]^-.2MeCN$ and $[C_5H_5NH]^+[LCu_4C\ell_{1.75}I_{3.25}]^-.2MeCN$ can be considered as isostructural or close to isostructural. In contrast to most calixresorcinarene derivatives, the cavity of **4**, which is normally available to a guest, is occupied by an anion and hence the solvent molecules are not included in the cavity of the bowl but occupy holes in the lattice formed by the calixresorcinarene molecules as illustrated in Figure 4. As in complex **4a**, the nitrogen atom of the pyridinium ring in **4d** could not be distinguished from the carbon atoms and hence a disorder of the nitrogen atom over all six sites was assumed. It has now been shown that the anion inclusion is selective and that the geometry imposed by the calixresorcinarene host can stabilize an unusual μ_4-face bridging binding mode of the guest halide.

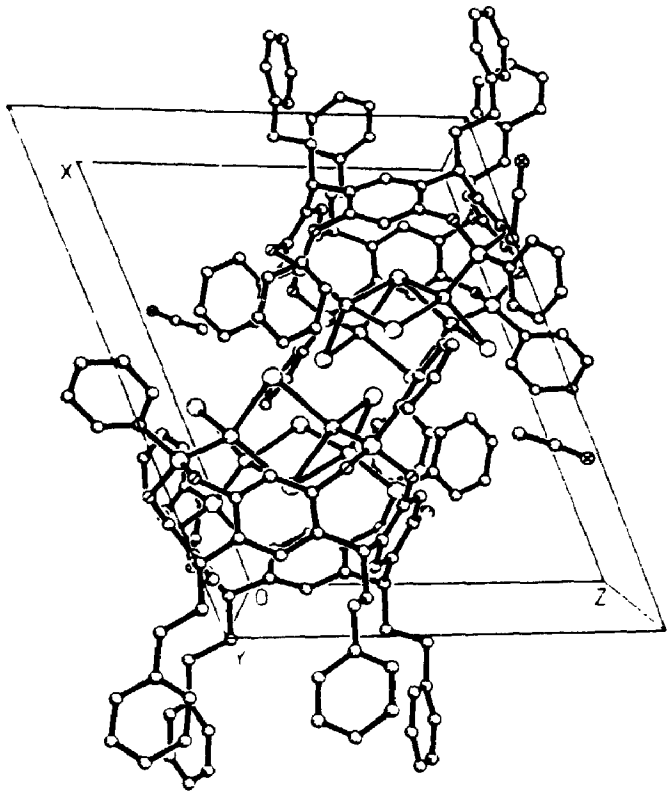


Figure 4. Unit cell packing of complex **4d**

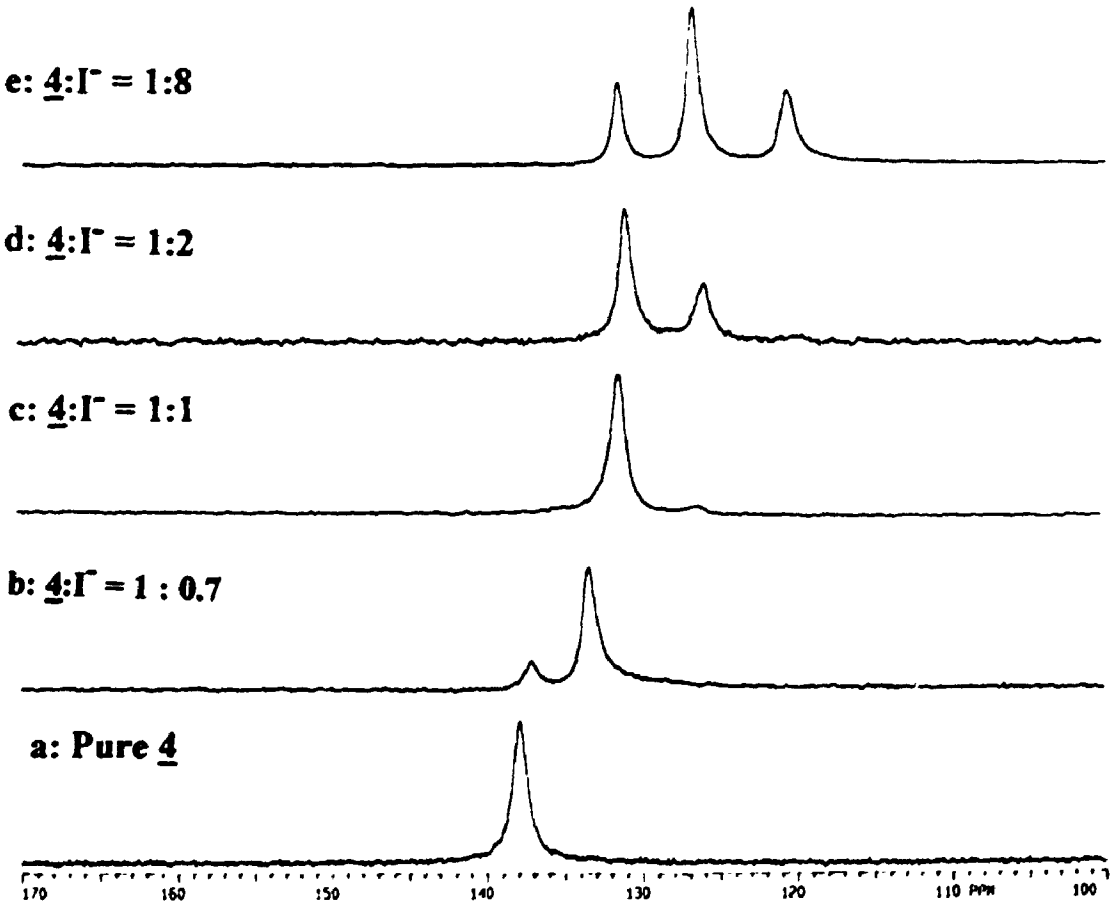


Figure 5. ^{31}P NMR spectra of complex **4a** and Bu_4NI in CD_2Cl_2 in different ratios at 25°C (Each sample was measured two hours after the sample preparation.)

The face bridging μ_4-I binding mode tor the included iodide in **4d** is rare in tetranuclear Cu(I) halide derivatives, although face bridging μ_4-Cl binding has been observed in some polynuclear species.[17] Why is it formed? We suggest that copper(I) has a thermodynamic preference for tetrahedral rather than trigonal planar stereochemistry and this can only be accommodated, given the ligand geometry, by the μ_4-halide binding in **4**. The chloride ligand is too small to bridge between all four copper(I) atoms for which the internuclear distances are controlled by the relatively rigid geometry of **2**, but it can bridge between three of them as in **4a**. On the other hand, iodide is large enough to bridge between all four copper atoms. Hence, in a mixed chloride-iodide complex, the iodide will bind selectively in the center as in **4d** and **4e** to form the more effective μ_4-face bridging bonds. It is less obvious why it is difficult to replace all the μ-Cl groups. The cavity size is determined by the $Cu_4(\mu\text{-}X)_4$ crown structure and this may be optimized for iodide inclusion or the formation of μ_4-face-bridged binding when a mixture of μ-I and μ-Cl ligands is present.

From the discussion above, it was concluded that I^- gives effective μ_4-face-bridged binding with four copper(I) centers. Will this effect lead to selective recognition of I^- over other anions by the complex **4a**? To test the selectivity of the anion inclusion, the complex **4a** and Bu_4NX (X = Br, I, CN or NO_3) were reacted in a 1:1 stoichiometric ratio in CD_2Cl_2. The occluded Cl^- of **4a** can be replaced selectively by Br^- or I^- as indicated by the presence of only a single resonance in the ^{31}P NMR spectrum (Figure 5). Thus only the replacement of the occluded Cl^- with Br^- or I^- will keep the geometry of the molecule in C_4 symmetry. Any replacement of chloride ligands on the rim will lead to

lower symmetry and so to more resonances in the ^{31}P NMR spectra. The CN^- and NO_3^- ions cannot replace the occluded Cl^-. Instead, excess Cl^- will decompose **4a**. These results can easily be explained, since the size of the cavity in **4** can accommodate Br^- and I^- and form the favoured μ_4-face bridged binding. When an excess amount of Bu_4NX (X=Br, I) was added to the solution of **4a**, partial replacement of the chloride ligands on the rim is also possible as indicated in Figure 5.

3.2.3 Silver(I) Rimmed Calixresorcinarenes

If the cavity size in **4** is determined by the $Cu_4(\mu\text{-}X)_4$ crown structure, it should be possible to optimize selectivity for anions of different sizes by using different transition metals. Furthermore, if the interpretation that the trapped μ_3-Cl migrates rapidly between the four copper atoms to give effective four-fold symmetry is correct, then a μ_4-Cl group should be possible even in the solution if copper(I) is replaced by a larger metal ion such as Ag(I). Reaction of **2** with $(AgCCPh)_n$ in the presence of pyridinium chloride gave a new complex $[C_5H_5NH]^+[\mathbf{2}.Ag_4(\mu\text{-}Cl)_4(\mu_4\text{-}Cl)]^-$, **5a**. As an alternative route to the preparation of **5a**, the reaction of $AgNO_3$ with **2** followed by addition of pyridinium chloride also gave **5a**, although in lower yield. The tendency to form **5a** was so strong that reaction of **3** with $Ag_2(\mu\text{-dppm})(NO_3)_2$ in the presence of pyridinium chloride also gave **5a** and $Ag_2(\mu\text{-dppm})_2(NO_3)_2$.[19]

The structure of **5a** is proposed to be the same as **4a** but with a μ_4-Cl ligand in place of the μ_3-Cl ligand in **4a**. The anion inclusion was readily proved by the presence of the

cation, $[C_5H_5NH]^+$ and by the observation of cation exchange reactions. The cation, $[C_5H_5NH]^+$ in **5** can be replaced by other bulky cations such as $n\text{-}Bu_4N^+$ and Me_4N^+ to give **5b** $[Me_4N]^+$ and **5c** $[n\text{-}Bu_4N]^+$. The isolation of complex **5** with different cations can also be achieved easily by carrying out the reaction of **2** with AgCCPh in the presence of the corresponding tetraalkylammonium chlorides, such as $n\text{-}Bu_4NCl$ and Me_4NCl. In addition, it was easier to replace all chlorides in **5a** with bromide or iodide to give the corresponding anions $[\mathbf{2}.Ag_4(\mu\text{-}X)_4(\mu_4\text{-}X)]^-$, (**5c**, $[n\text{-}Bu_4N^+]$, X = I; **5d**, $[C_5H_5NH]^+$, X = Br; **5e**, $[C_5H_5NH]^+$, X = I) than in **4a**.

The structure of **5** was eventually proved by an X-ray structure analysis on complex **5b**. As expected, a μ_4-Cl unit is indeed present as is illustrated in figure 6. The distances Ag-μ-Cl (2.56(1)-2.62(1) Å) are shorter than Ag-μ_4-Cl (2.69(1)-2.76(1) Å), and hence presumably stronger bonding is present.[20] The bond distances and angles are listed in Table 3.

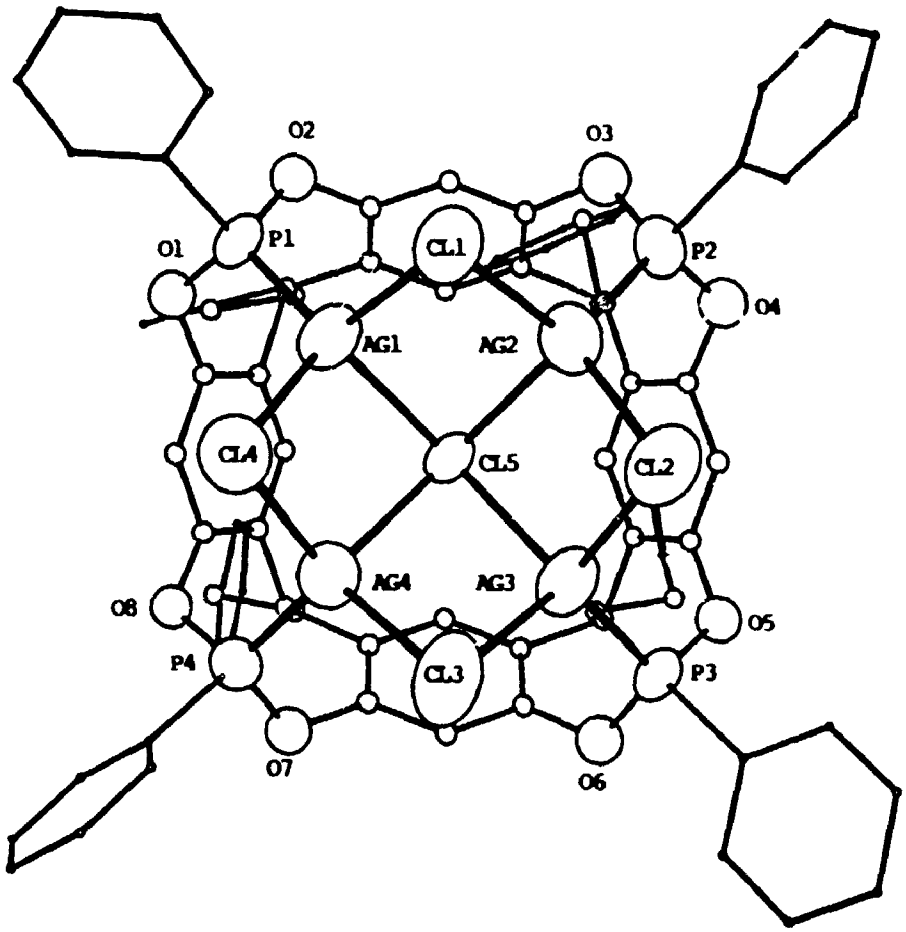


Figure 6. A front view of the molecular structure of **5b**. The phenyl rings on both PhP- and -CH_2CH_2Ph groups and hydrogen atoms have been omitted for clarity.

Table 3. Selected bond distances (Å) and angles (°) of **5b**

(a) Selected bond distances (Å)

Ag(1)-Cl(1)	2.559(12)	Ag(2)-Cl(1)	2.586(12)	Ag(2)-Cl(2)	2.585(13)
Ag(3)-Cl(2)	2.598(13)	Ag(3)-Cl(3)	2.619(13)	Ag(4)-Cl(3)	2.594(13)
Ag(1)-Cl(4)	2.574(12)	Ag(4)-Cl(4)	2.609(13)	Ag(1)-Cl(5)	2.722(10)
Ag(2)-Cl(5)	2.756(10)	Ag(3)-Cl(5)	2.687(10)	Ag(4)-Cl(5)	2.691(10)
Ag(1)-P(1)	2.411(11)	Ag(2)-P(2)	2.401(11)	Ag(3)-P(3)	2.390(11)
Ag(4)-P(4)	2.368(12)	P(1)-O(1)	1.630(24)	P(1)-O(2)	1.596(23)
P(2)-O(3)	1.628(26)	P(2)-O(4)	1.646(24)	P(3)-O(5)	1.604(22)
P(3)-O(6)	1.642(23)	P(4)-O(7)	1.625(24)	P(4)-O(8)	1.643(23)

(b) Selected bond angles (°)

Cl(1) -Ag(1) -P(1)	114.6(4)	Cl(4) -Ag(1) -P(1)	114.3(4)
Cl(4) -Ag(1) -Cl(1)	108.5(4)	Cl(5) -Ag(1) -P(1)	122.1(3)
Cl(5) -Ag(1) -Cl(1)	96.4(4)	Cl(5) -Ag(1) -Cl(4)	98.4(4)
Cl(1) -Ag(2) -P(2)	115.8(4)	Cl(2) -Ag(2) -P(2)	115.7(4)
Cl(2) -Ag(2) -Cl(1)	111.8(4)	Cl(5) -Ag(2) -P(2)	119.3(3)
Cl(5) -Ag(2) -Cl(1)	94.9(3)	Cl(5) -Ag(2) -Cl(2)	96.2(4)
Cl(2) -Ag(3) -P(3)	114.2(4)	Cl(3) -Ag(3) -P(3)	114.7(4)
Cl(3) -Ag(3) -Cl(2)	108.8(5)	Cl(5) -Ag(3) -P(3)	122.5(3)
Cl(5) -Ag(3) -Cl(2)	97.6(4)	Cl(5) -Ag(3) -Cl(3)	96.7(4)
Cl(3) -Ag(4) -P(4)	113.8(5)	Cl(4) -Ag(4) -P(4)	113.6(4)
Cl(4) -Ag(4) -Cl(3)	110.9(4)	Cl(5) -Ag(4) -P(4)	121.1(3)
Cl(5) -Ag(4) -Cl(3)	97.2(4)	Cl(5) -Ag(4) -Cl(4)	98.3(3)
Ag(2) -Cl(1) -Ag(1)	86.4(3)	Ag(3) -Cl(2) -Ag(2)	84.3(4)
Ag(4) -Cl(3) -Ag(3)	83.6(4)	Ag(4) -Cl(4) -Ag(1)	82.4(3)
Ag(2) -Cl(5) -Ag(1)	80.1(3)	Ag(3) -Cl(5) -Ag(1)	130.7(4)
Ag(3) -Cl(5) -Ag(2)	79.4(3)	Ag(4) -Cl(5) -Ag(1)	78.2(3)
Ag(4) -Cl(5) -Ag(2)	128.4(4)	Ag(4) -Cl(5) -Ag(3)	80.5(3)
O(1) -P(1) -Ag(1)	115.6(9)	O(2) -P(1) -Ag(1)	114.6(10)
O(2) -P(1) -O(1)	104.9(12)	C(111)-P(1) -Ag(1)	116.1(15)
C(111)-P(1) -O(1)	102.6(18)	C(111)-P(1) -O(2)	101.1(16)
O(3) -P(2) -Ag(2)	116.4(10)	O(4) -P(2) -Ag(2)	116.5(9)
O(4) -P(2) -O(3)	103.7(13)	C(211)-P(2) -Ag(2)	123.6(11)
C(211)-P(2) -O(3)	95.9(14)	C(211)-P(2) -O(4)	96.7(15)
O(5) -P(3) -Ag(3)	116.1(9)	O(6) -P(3) -Ag(3)	113.5(9)
O(6) -P(3) -O(5)	104.8(12)	C(311)-P(3) -Ag(3)	122.3(11)
C(311)-P(3) -O(5)	97.5(13)	C(311)-P(3) -O(6)	99.9(13)
O(7) -P(4) -Ag(4)	115.5(9)	O(8) -P(4) -Ag(4)	117.1(9)
O(8) -P(4) -O(7)	103.3(12)	C(411)-P(4) -Ag(4)	117.9(12)

Although the geometry of **2** is relatively rigid, the cavity size is still flexible and can be adjusted by moving the phosphorus atoms outward or inward. When Cu(I) atoms were replaced by larger Ag(I) atoms, the P...P distances increased to fit the larger metal atoms, while still allowing the effective μ_4-X face-bridged bonding (Table 4). When μ_4 bridging chloride ligands were replaced by larger anions such as iodide, the M...M distance increased to leave more space for the larger anion inclusion.

Table 4. Selected non-bonding interatomic distances (Å)* of **4a**, **4d** and **5a**

		P...P	M...M	Cl...Cl
$C_{89}H_{74}N_1Cu_4Cl_5P_4O_8.2CH_3CN$	**4a**	6.04(1)	3.33(1)	3.74(1)
$C_{89}H_{74}N_1Cl_{1.75}Cu_4I_{3.25}P_4O_8.2CH_3CN$	**4d**	6.09(1)	3.37(1)	4.23(2)**
$C_{88}H_{80}N_1Ag_4Cl_5P_4O_8.1.5C_2H_5CN.CH_2Cl_2$	**5b**	6.29(1)	3.48(2)	4.24(2)

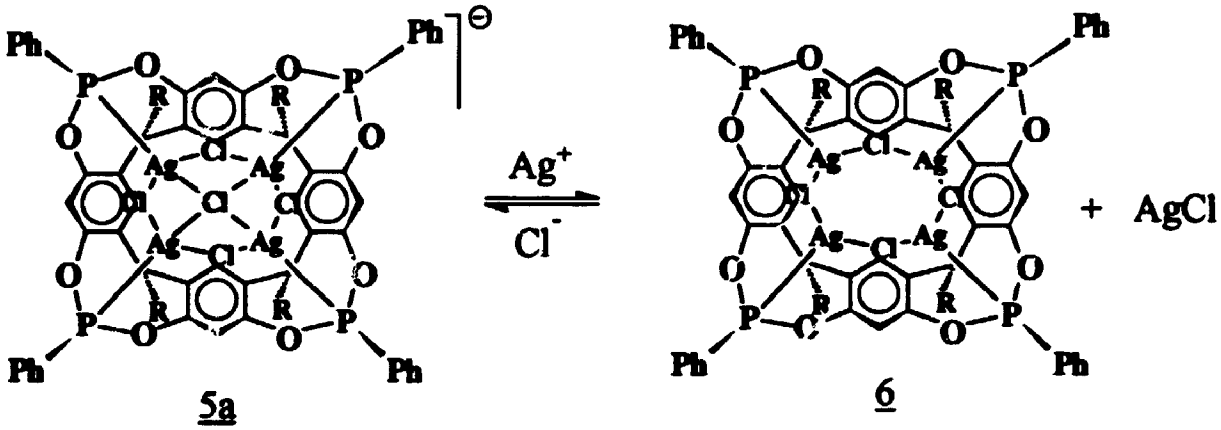
* The interatomic distances listed here are mean values.

** The interatomic distance of X (Cl, I mix)

3.2.4 Anion Recognition Driven by the μ_4-Face-bridged Binding

From the supramolecular chemistry point of view, it is crucial to know whether the anion inclusions are reversible and selective. Two experiments have been designed to test the reversibility and selectivity of anion inclusion in complex **5a**. When complex **5a** was treated with silver(I) nitrate salt in 1:1 ratio, the occluded chloride anion can be removed selectively to give **6**. Reaction of a solution containing **6** with a solution containing Cl^-, gave **4a** again as illustrated in Figure 7. The whole process can be monitored easily by observation of the presence or absence of pyridinium cation peaks in the ^1H NMR spectra and by chemical shift changes in the ^{31}P NMR spectra as shown in Figure 8. It is

interesting to note, however, that a different result was obtained when the copper(I) derivative **4a** was treated with $AgNO_3$/MeCN solution. The silver(I) did not remove the occluded chloride to give a precipitate of AgCl Instead, the silver(I) replaced the copper(I) to form **5a**, which was identified by spiking with an authentic sample. This experiment gives a further evidence that the μ_4-face-bridged binding, which is present in **5a** but not in **4a**, is favoured in this particular cluster system.



5a 6

Figure 7. Reversibility of anion inclusion of **5a**

As with **4a**, complex **5a** can also recognize different anions and selectively include them in its cavity. When Bu_4NX (X = Cl, I, CN, NO_3) were reacted with **5a** in a 1:1 stoichiometric ratio, only I^- could replace Cl^- and was selectively included. The priority of iodide inclusion is clearly indicated by the ^{31}P NMR spectra illustrated in Figure 9. When **5a** and I^- were mixed in a 1:1 ratio, only the occluded Cl^- was replaced by I^-, whereas excess I^- led to replacement of chlorine ligands on the rim also.

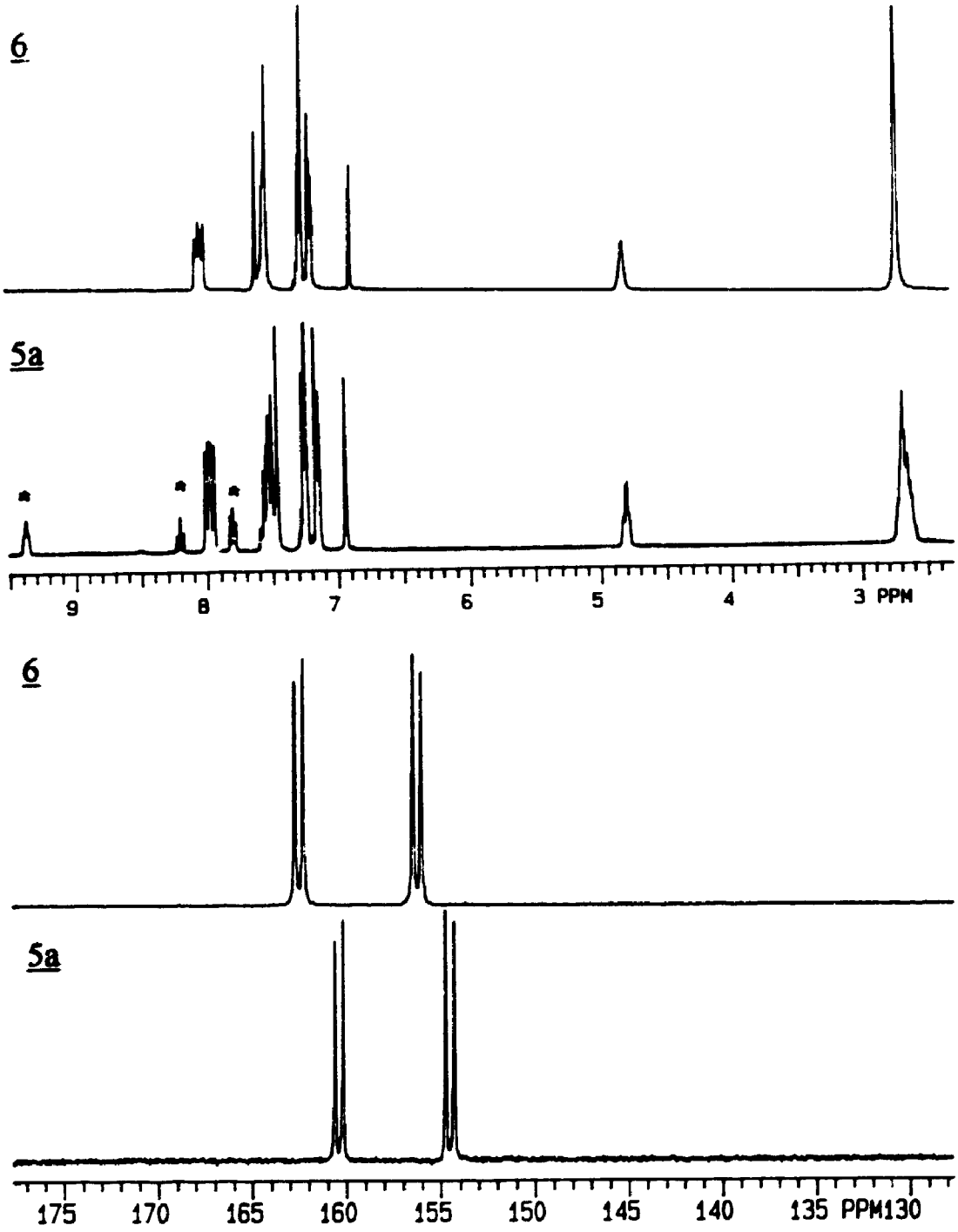


Figure 8. ^{1}H and ^{31}P NMR spectra of **5a** and **6** showing the differences between complexes with and without anion inclusion respectively (notice in **6**, there are no pyridinium cation resonances which are marked with an asterisk in **5a**)

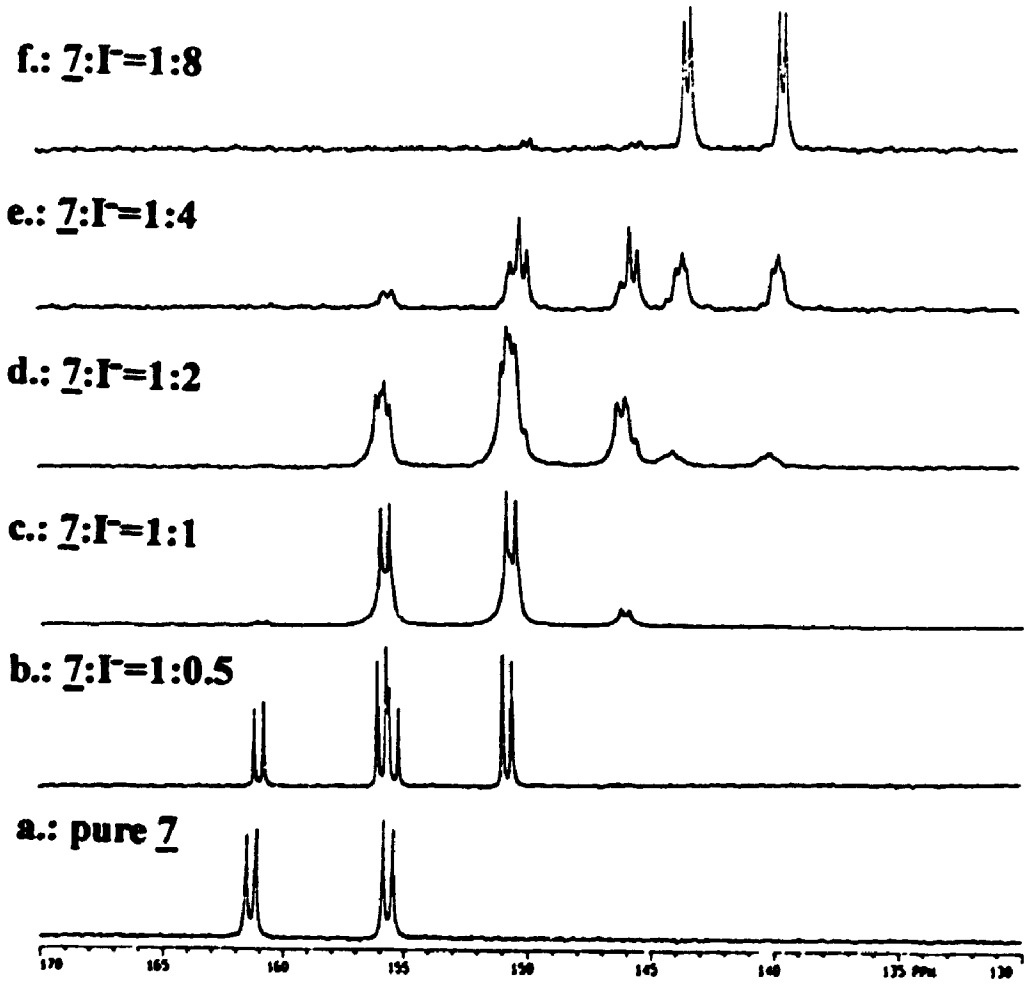


Figure 9. ^{31}P NMR spectra of complex 5a and Bu_4NI in CD_2Cl_2 in different ratios at 25° showing the selective iodide inclusion.

3.2.5 Model System for Anion Inclusion

When the occluded anion of complex **5a** was removed by $AgNO_3$, it actually gave a compound **6** with an empty cavity defined by a set of electron-deficient transition metals on the upper rim of the calixresorcinarene bowl. Does the compound **6** act as an anion receptor? Treatment of **6** with Bu_4NI in a 1:1 ratio gave the I^- inclusion complex **7**, identical to the compound obtained by the anion exchange reaction of **5a** with I^- (Figure 9). The structure of **7** is expected to be the same as for **5a** but with an I^- anion encapsulated in its cavity in C_4 symmetry. When complex **6** was treated with $(Me_3Sn)_2S$ in a 1:1 ratio in $CHCl_3$, it gave a clean product **8**. The ^{31}P NMR spectrum of **8** showed only one resonance, which appeared as two doublets due to ^{109}Ag and ^{107}Ag coupling, suggesting that S^{2-} was included selectively in the cavity without any rim chloride ligands replacement, which would lead to lower symmetry and hence to more complicated resonances. it is well-known that the coupling constant ^1J(Ag-P) decreases as the coordination number at silver(I) increases. The coupling constant of complex **8** decreased significantly from $^1J(^{109}Ag\text{-}^{31}P)$ = 823Hz in the anion receptor **6** to $^1J(^{109}Ag\text{-}^{31}P)$ = 673Hz in the complex **8**, which is consistent with the conclusion that the S^{2-} anion was included selectively by interaction with four Ag(I) centers. Details of chemical shift and coupling constant changes are listed in Table 5. The S^{2-} anion cannot replace I^- in **7** whereas it can partly replace occluded Cl^- in **5a**, although the equilibrium is still tilted towards Cl^- inclusion. Clearly, the binding of I^- with four Ag(I) atoms is much stronger than that of either S^{2-} or Cl^-.

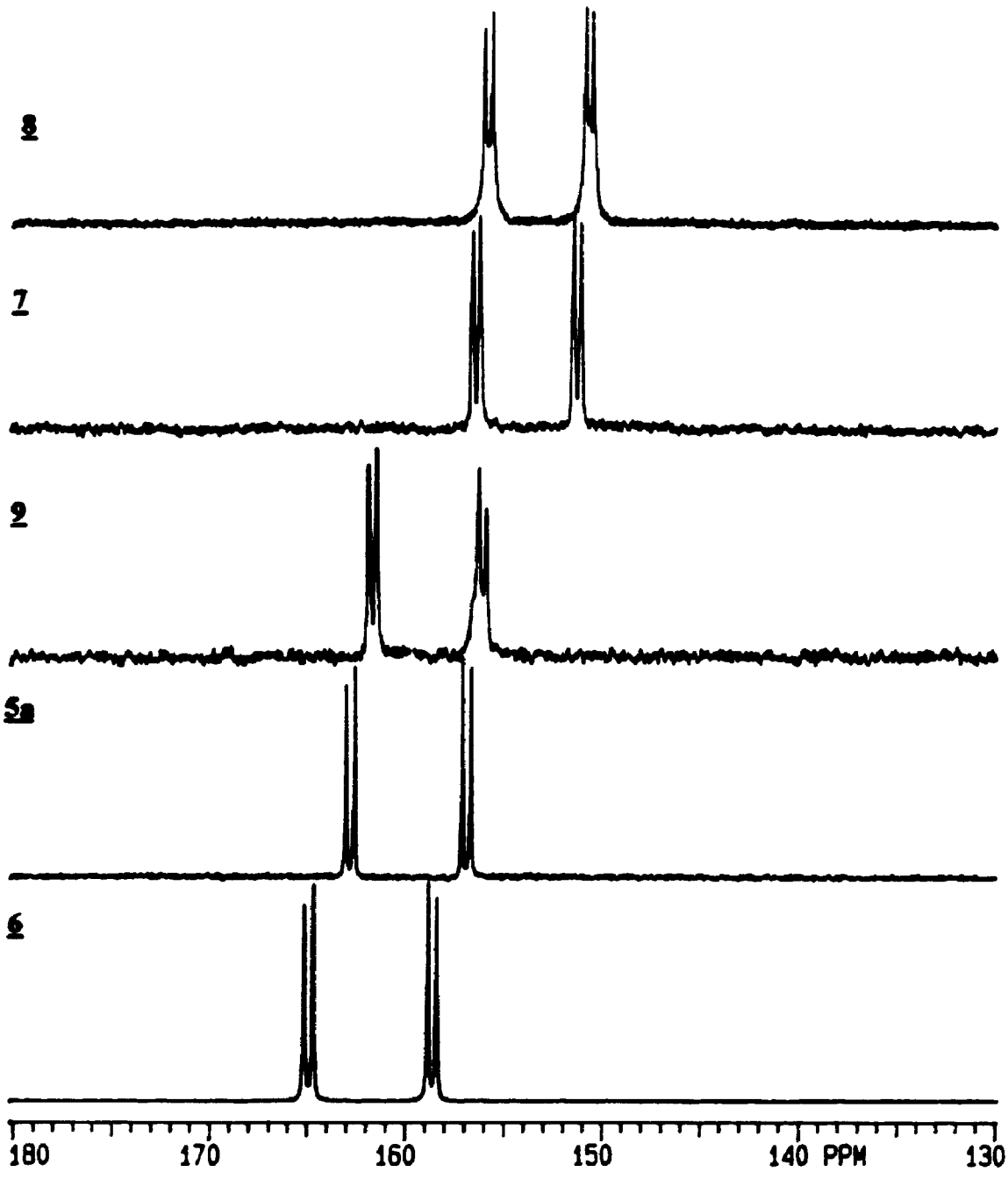


Figure 10 ^{31}P NMR Spectra of 6, 5a, 7, 8 and 9 showing the anion inclusions

Furthermore, if **6** and Bu_4NCN were mixed in a 1:1 ratio in $CHCl_3$ solution, it gave another clean product **9**. A similar decrease in $^1J(Ag-P)$ values was observed as in the formation of **8** (Figure 10). The CN- anion is also expected to be included in the cavity by interaction with Ag(I) atoms, although the interactions may be fluxional between the four Ag(I) centers. Therefore, it could be concluded that compound **6** acted as a powerful anion receptor towards small guests such as CN^-, Cl^-, Br^-, I^- or S^{2-} in solution

Table 5. ^{31}P NMR chemical shifts and coupling constants of **6**, **5a**, **7**, **8** and **9** in $CDCl_3$ at room temperature

	6	**5a**	**7**	**8**	**9**
Included Anions	---	Cl^-	I^-	S^{2-}	CN^-
δ (ppm)	161.9	157.0	153.9	153.4	158.9
$J(^{109}Ag-^{31}P)$ Hz	822.5	766.3	667.2	673.3	723.4
$J(^{107}Ag-^{31}P)$ Hz	712.5	664.1	578.6	584.7	627.2

3.2.6 Nature of the Unusual μ_4-face-bridged Binding

It is clear from the above discussion that anion inclusion is favoured by formation of the unusual μ_4-face-bridged binding. The nature of the unusual $M_4(\mu_4-X)$ bond in **4** and **5** was studied by carrying out Extended Huckel MO calculations.[21] The model complex $[Ag_4(\mu-Cl)_4(\mu_4-Cl)(PH_3)_4]^-$, **A**, was considered to be formed from the fragment $[Ag_4(\mu-Cl)_4(PH_3)_4]$, **B**, by coordination of Cl^-. Both **A** and **B** were built up with ideal C_{4v} symmetry by using average distances and angles based on the X-ray structure determination. Bonding interactions are readily identified by overlap of filled orbitals of Cl^- with acceptor orbitals on silver. There are only three net σ-bonding interactions ($a_1 + 2e$). Since one of the

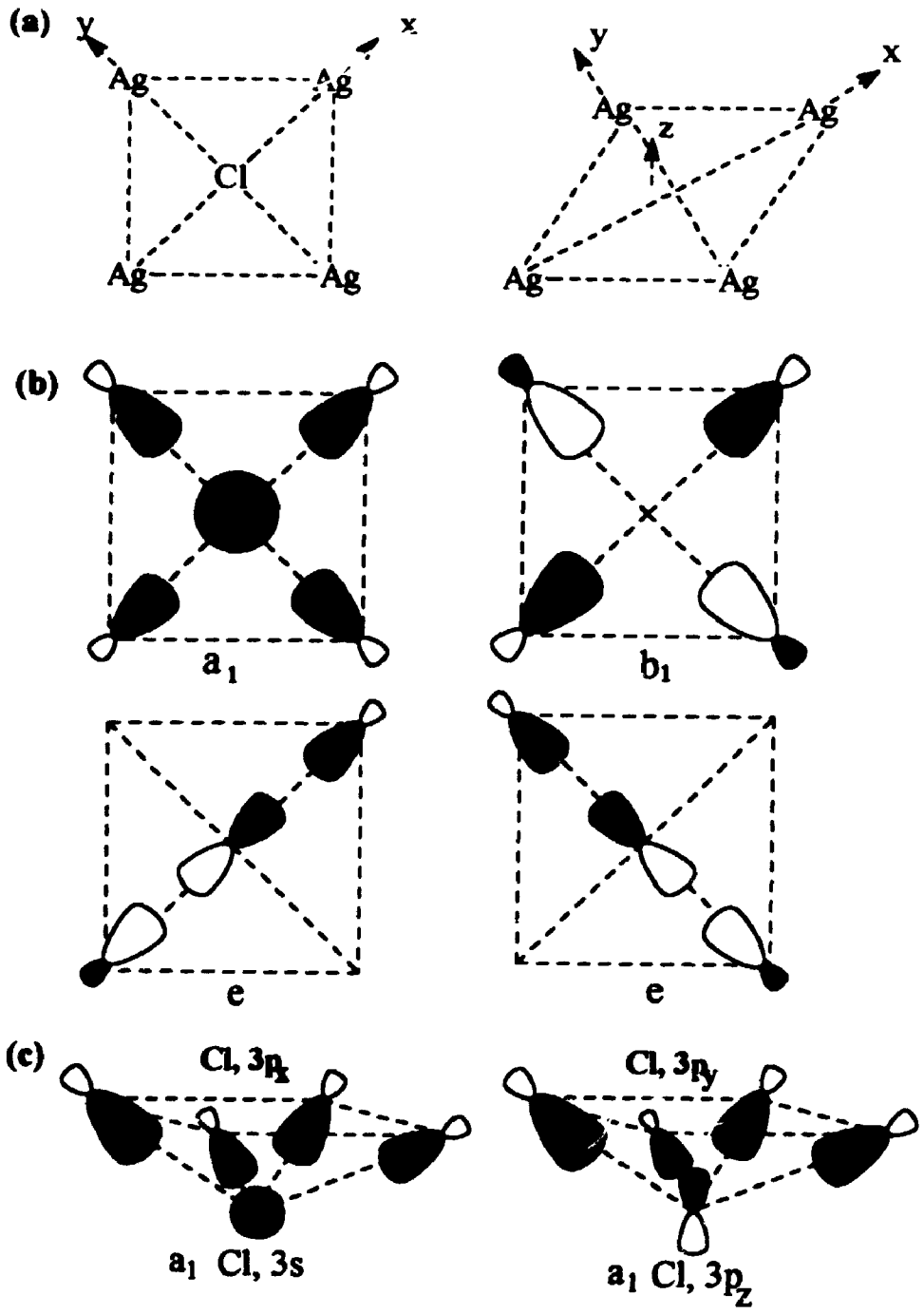


Figure 11. A schematic view of the overlap between the symmetry adapted acceptor orbitals on Ag with the donor orbitals of Cl^-. The b_{1u} acceptor orbital is the LUMO in the model complex **A**.

four sets of acceptor orbitals (b_{1u}, LUMO in **A**) is non-bonding (Figure 11), the maximum $Ag_4(\mu_4\text{-}Cl)$ total bond order is three rather than four, consistent with the longer Ag-μ_4-Cl distance (average 2.718 Å) compared to the single-bond Ag-μ-Cl distance (average 2.585 Å).[20] The calculated charge on the μ_4-Cl ligand in **A** is -0.498e, indicating that the μ_4-Cl^- ligand is not simply a guest anion but is covalently bonded to the silver(I) centers.[21]

3.2.7 Aliphatic Nucleophilic Substitution involving the Occluded Cl^-

It is well established that halide exchange, a type of aliphatic nucleophilic substitution, in aprotic solvents follows the S_N2 mechanism with inversion of configuration at carbon as illustrated in Figure 12.[22] The reactivity of the alkyl halides follows the order primary > secondary >> tertiary. The reaction is most often applied to the preparation of alkyl iodide from alkyl chloride. However, the halide exchange is an equilibrium process and this limits its applications.

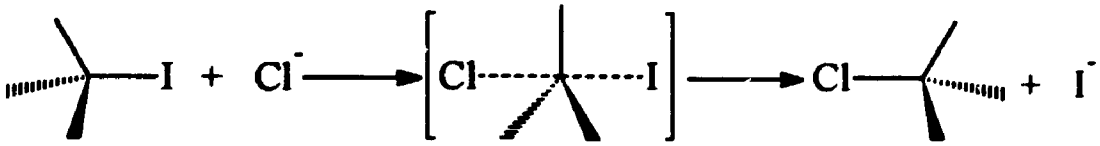


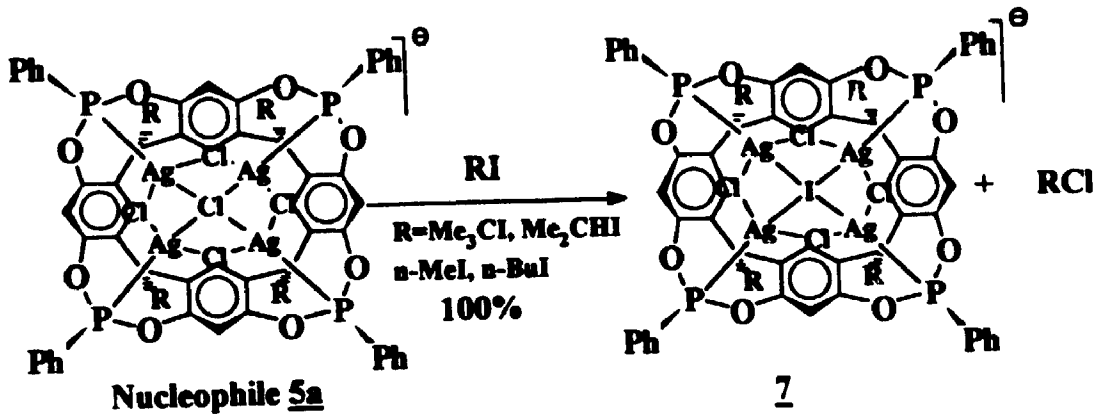
Figure 12. S_N2 mechanism of alkyl halide exchange in an aprotic solvent

In previous sections, it was demonstrated that a halide anion can be included in the cavity defined by a set of transition metal atoms on the upper rim of a calixresorcinarene bowl and that I^- has precedence over other halide ions for inclusion in the cavity. Therefore,

it will be interesting to find out the nucleophilic activity of occluded Cl^- toward alkyl iodide. This should lead to formation of an alkyl chloride and occluded iodide, and the equilibrium should be shifted by the preference for iodide inclusion.

Thus the aliphatic nucleophilic substitution of alkyl iodides with **5a** was investigated. Treatment of 2-methyl-2-iodopropane with anion occluded **5a** in a 1:1 ratio gave **7** and 2-methyl-2-chloropropane with 100% conversion at 20°C in 5 minutes. The reaction of 2-iodopropane and **5a** in a 1:1 ratio proceeded very slowly to give **7** and 2-chloropropane at room temperature. It took about 10 days to reach 100% conversion at 20°C. However, the reaction speeded up at 30°C with a stoichiometric 1:25 ratio of 2-iodopropane and **5a**, and the reaction can be followed easily by NMR techniques as illustrated in Figure 13. As mentioned before, the halide exchange is an equilibrium process, and it is rare that a halide exchange reaction between RI and Cl^- can reach 100% conversion. For example, the equilibrium constant (K) of reaction between [PPN]Cl and 2-iodopropane in $CDCl_3$ was measured by us. It gave a K = 0.30 with only 35.3% conversion. Apparently, the precedence of I^- over Cl^- to form effective μ_4-face bridged bonding accounts for the driving force for the 100% conversion.

When different iodoalkanes were used to perform the same aliphatic nucleophilic substitution with **5a** as a nucleophile, it was found that the reactivity of iodoalkane toward **5a** follows the sequence tertiary > secondary >> primary, just the opposite of the normal halide exchange reaction rate sequence as Table 6 shows. How does this happen? One possible mechanism is that the reagent RI attacks two Ag(I) centres first, forming a



Reaction Rates: Me_3CI > Me_2CHI >> n-BuI ~ MeI

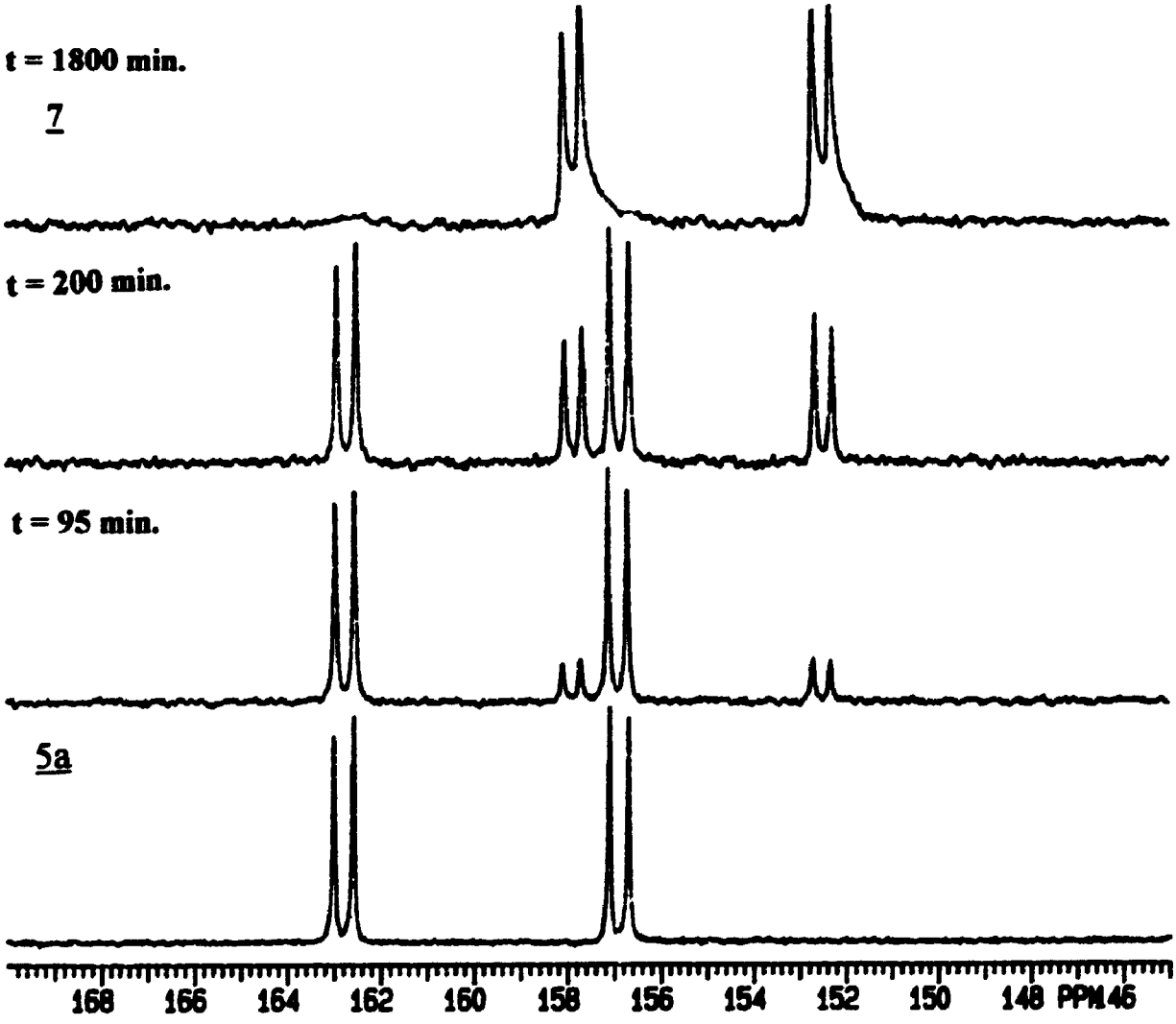


Figure 13. Reaction of 5a with Me_2CHI in 1:25 stoichiometric ratio and the ^{31}P NMR spectral changes against time at 30°C in CD_2Cl_2

weak μ_2 bond, and the occluded μ_4-Cl may then form a μ_2 bonds with the other two Ag(I) centres. Then the μ_2-Cl and μ_2-I exchange may occur as illustrated in Figure 14. Finally, the μ_2-I forms more effective μ_4-I bonds with four Ag(I) centres and so replaces the original μ_4-Cl ligand.

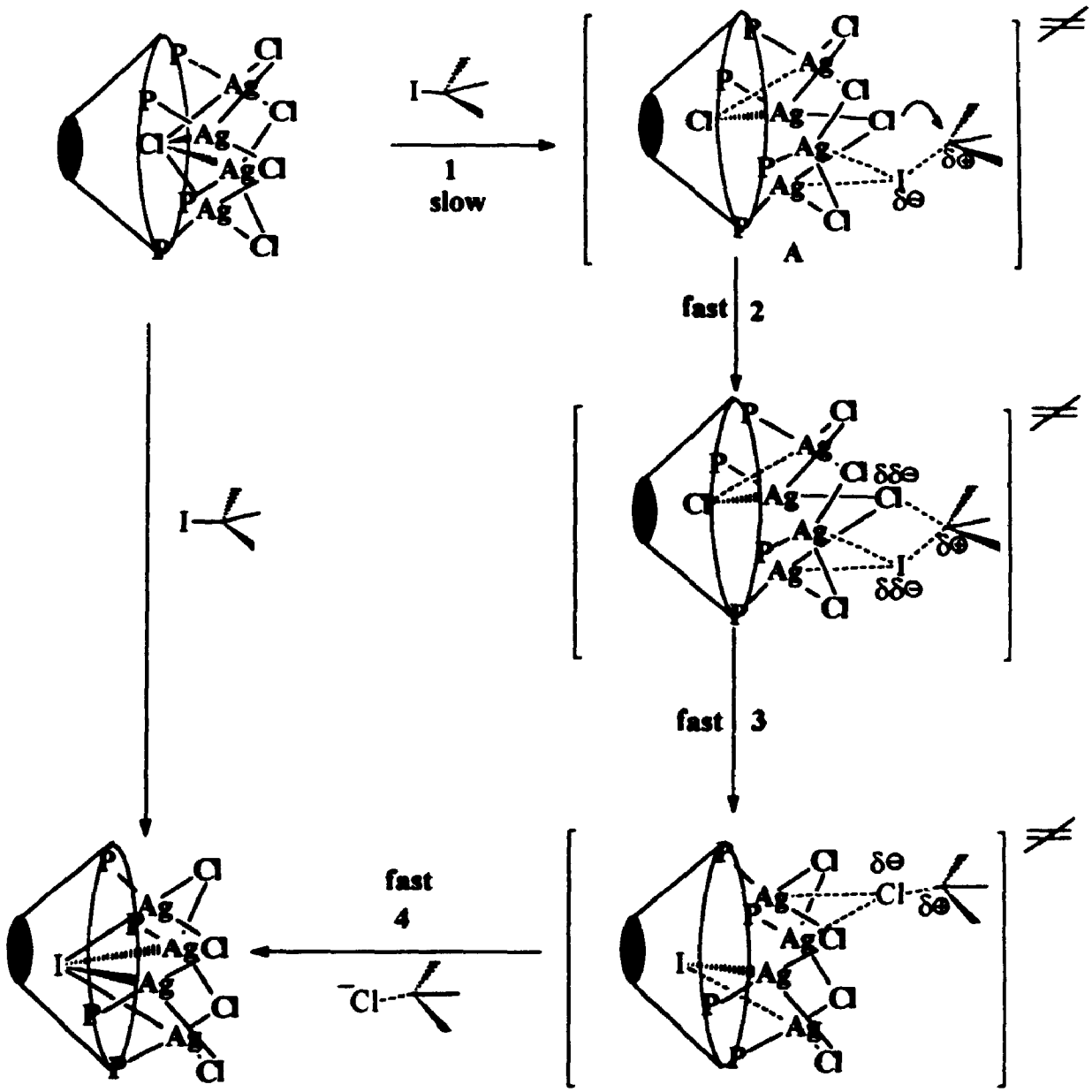
Table 6. Activity of different iodoalkanes towards the nucleophile **5a**[*]

Time(min.)	tertiary Me_3CI	Secondary Me_2CHI	Primary MeI
5	100%	1%	0[**]
850	100%	7.9%	<1%
3080	100%	32.6	~1%

* The experiments were carried out with 1:1 stoichiometric ratios of iodoalkane and **5a** at room temperature in CD_2Cl_2

** No trace of MeCl could be detected by ^1H NMR technique at this stage.

If the mechanism proposed for aliphatic nucleophilic substitution by **5a** is true, an analogous mechanism will be expected for anion exchange of **5a** with Bu_4NI as illustrated in Figure 15. Since the anion exchange reaction is very fast, the steps 2-4 in Figure 14 are expected also to be very fast and therefore step 1 is the rate determining step. The easier the dissociation of the R-I bond, the faster it will be to form intermediate A and the faster the reaction. This is consistent with the reactivity order: tertiary > secondary > primary as observed. Based on this proposed mechanism, it is easy to predict that the aliphatic nucleophilic substitution of **5a** with RI will follow second order kinetics with retention of configuration at chiral carbon.



Predictions: 1. Second order kinetics
2. Configuration retention of alkyl halides

Figure 14. Proposed mechanism for aliphatic nucleophilic substitution by 5a

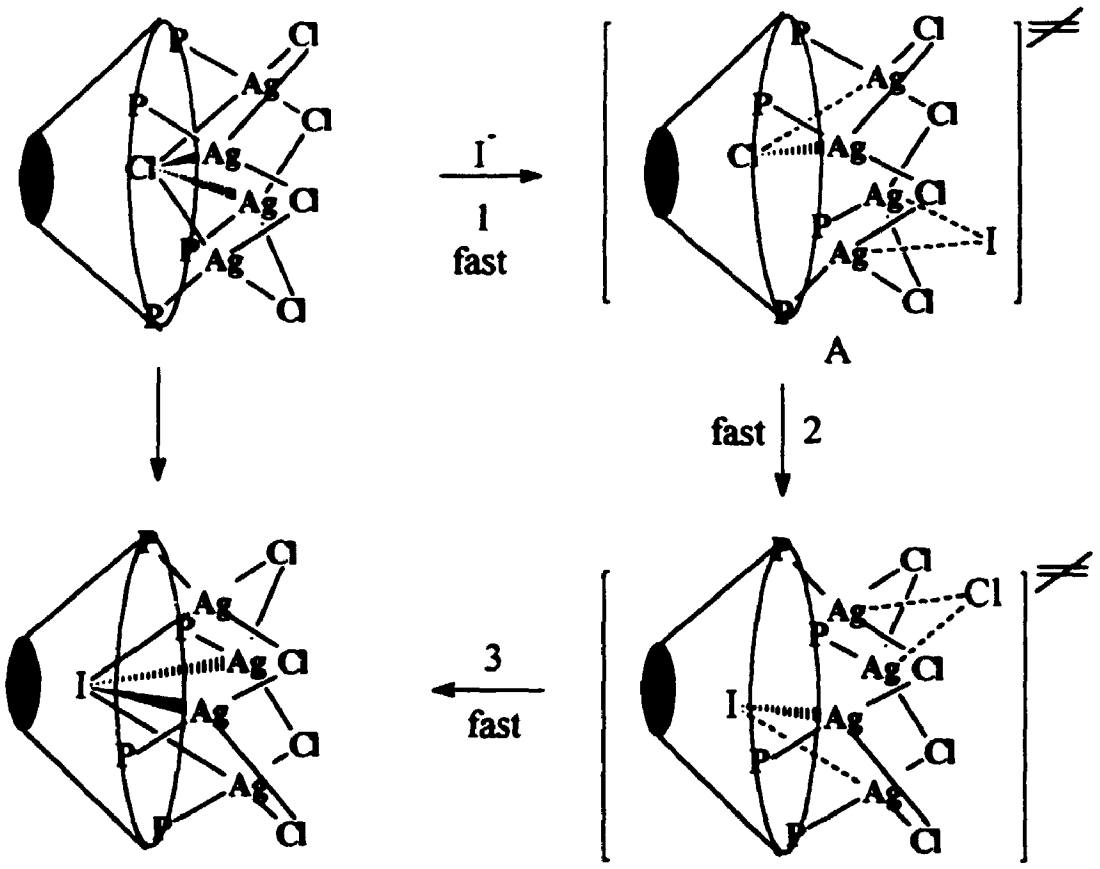


Figure 15. Proposed mechanism for anion exchange of **5a** with Bu_4NI

When the reaction of **5a** with 2-iodopropane was carried out in 1 : 100 stoichiometric ratio, pseudo-first order kinetics were observed as shown in Figure 16. When the stoichiometric ratio of starting materials was changed from 1:83 to 1:60 and 1:25, pseudo-first order kinetics were still observed, and a plot of the first order rate constants versus [i-PrI] was linear and passed through the origin as illustrated in Figure 17. Hence the reaction rate is first order in both [**5a**] and [i-PrI]. Therefore, the kinetic data are fully consistent with the proposed mechanism. The kinetic evidence is a necessary but not a sufficient condition for the mechanism to be correct. Much more convincing evidence

should come from the fact the mechanism predicts retention of configuration when substitution occurs at a chiral carbon. However, this experiment has not yet been finished due to lack of an optically active alkyl iodide.

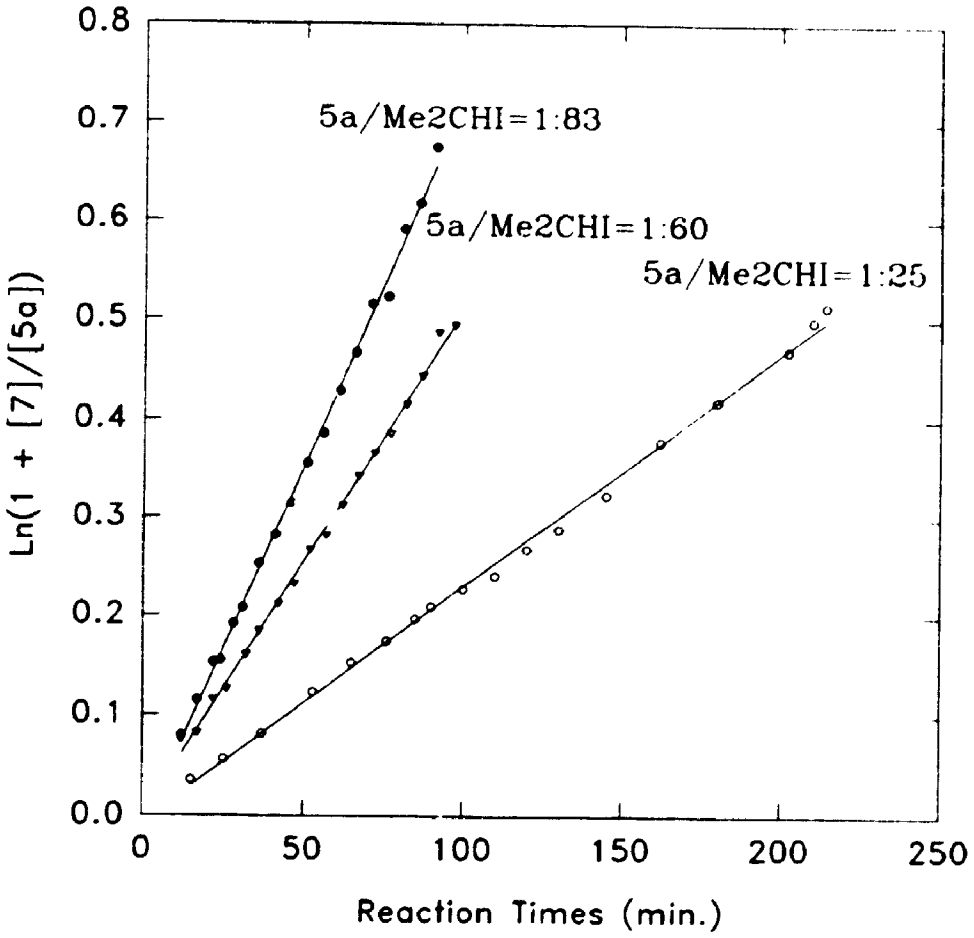


Figure 16. ln([7]/[5a] + 1) *vs* time (t) showing pseudo-first order kinetics

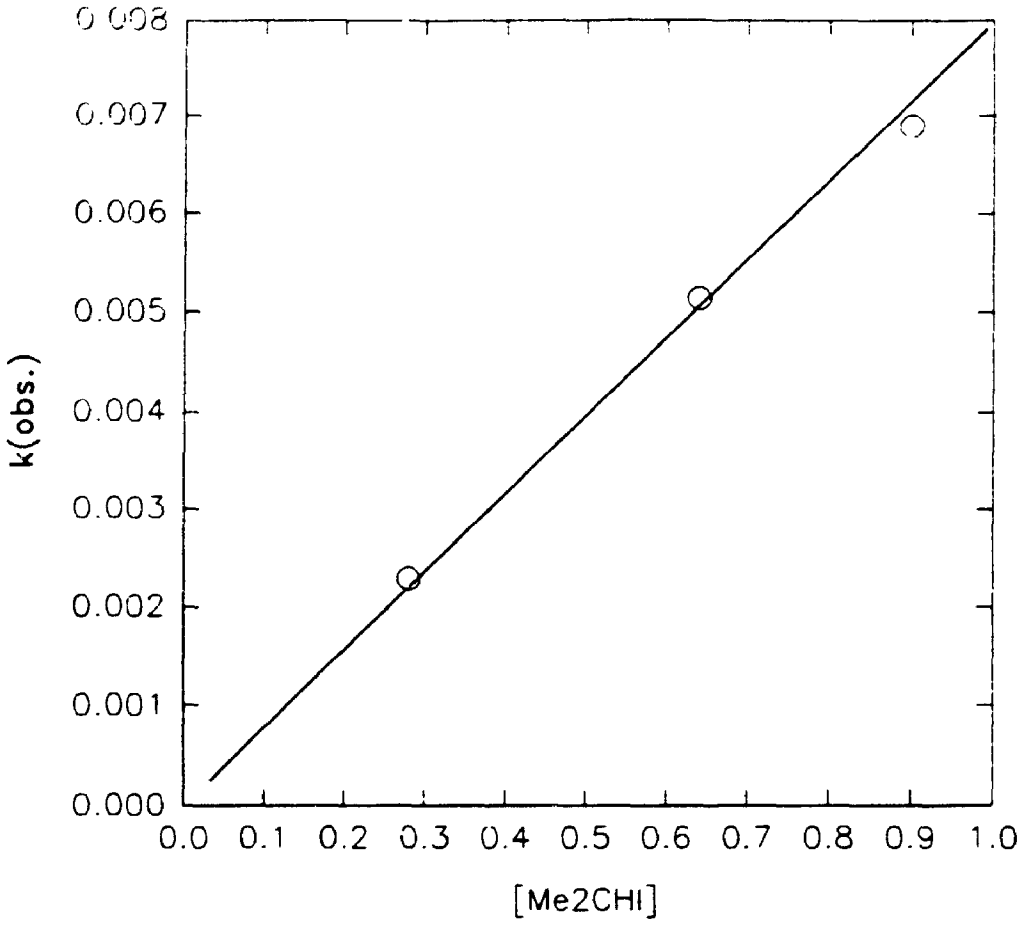


Figure 17. **The pseudo-first order rate constants k *vs* [i-PrI]**

3.3 CONCLUSION

The multidentate complexation of an anion by a neutral host containing transition metal substituents at the rim of macrocyclic ligand opens up a realm of chemistry that is distinct from the chemistry of positively charged hosts. This work has demonstrated how transition metal rimmed complexes of a phosphonitocalixresorcinarene can provide a host for the size-selective inclusion of anions which are stabilized by a unique μ_4-face-bridged

binding mode. The nucleophilic properties of the imprisoned anion are dramatically changed. The novel anion receptor system could have applications in several areas such as anion extraction and aliphatic nucleophilic substitution with 100% conversion.

3.4 EXPERIMENTAL SECTION

The complexes calixresorcinarene,[23] $[CuCCPh]_n$,[24] $[AgCCPh]_n$,[24] were prepared by literature methods and tetraphosphonito-calixresorcinarene **2** was prepared as described in the previous chapter. All the experiments were carried out at the conditions described in the previous chapter 2. All the spectroscopic data were recorded on the same instruments listed in Chapter 2 by the same methods. The crystal structures were solved by Dr. J. J. Vital. Data were obtained by using an Enraf Nonius CAD4F diffractometer with graphite monochromator and MoKα radiation at λ = 0.71073 Å wavelength.

3.4.1 Preparation of **4a**

A mixture of $[CuCCPh]_n$ (0.g, 0.61mmol), pyridinium chloride (0.07g, 0.6mmol) and tetraphosphonito-calix[4]resorcinarene, **2**, (0.20g, 0.15mmol) in CH_2Cl_2 was stirred at room temperature for 15h to give a clear solution. The CH_2Cl_2 and HCCPh were removed completely under vacuum. The residue was redissolved in CH_2Cl_2 (4mL). After filtration, the solution was crystallized by diffusion with MeCN (10mL). A white solid **4a** was obtained, which was washed with MeCN and dried under vacuum. Yield: 0.21g, 76.1%. Anal. Calc for **4a** $C_{89}H_{74}Cl_5Cu_4N_1O_8P_4$: C,58.2; H,4.1; Found: C, 58 3; H, 4 4%

NMR in CD_2Cl_2: $\delta(^{31}P)$ = 134.9 [s, br]; $\delta(^1H)$ 2.75 [br, 16H, C<u>H</u>$_2$C<u>H</u>$_2$Ph], 4.85 [br, 4H, C<u>H</u>(CH$_2$)$_2$Ph], 7.01 [t, $^4J_{PH}$ = 2.0Hz, 4H, Ar<u>H</u>, ortho to O], 7.20-7.34 [m, 20H, C$_6$<u>H</u>$_5$], 7.52 [s, 4H, Ar<u>H</u>, meta to O], 7.53-7.67 [m, 12H, PC$_6$<u>H</u>$_5$, para and meta to P], 8.02-8.14 [m, 8H, PC$_6$<u>H</u>$_5$, ortho to P]. 8.28 [t, 2H, C$_5$<u>H</u>$_5$NH$^+$, ortho to N], 7.67-7.80 [m, 3H, C$_5$<u>H</u>$_5$NH$^+$, meta and para to N], 9.25 [s, br, 1H, C$_5$H$_5$N.<u>H</u>$^+$]; IR: ν_{NH} = 3500cm^{-1} (w).

3.4.2 Crystallographic Data for <u>4a</u>

The crystals of <u>4a</u>, which were suitable for X-ray analysis, were obtained by slow diffusion MeCN (20mL) into a CH_2Cl_2 (2mL) solution of <u>4a</u> (150mg). The colourless crystals lose solvent and become opaque on exposure to the atmosphere and hence were examined under a mixture of paraffin oil and the mother liquor. A suitable quality and size crystal was wedged inside a Lindemann capillary. Both ends of the capillary were flame sealed immediately and it was then mounted for data collection. Molecular Formula: $C_{89}H_{74}Cl_5Cu_4N_1O_8P_4.2CH_3CN$; Formula Weight: 1921.5; Space group: Triclinic, P1bar; Cell dimensions: a = 17.511(4)Å, b = 21.479(4)Å, c = 13.253(2)Å, α = 101.52(1)°, β = 111.94(1)° γ = 82.14(2)°, V = 4519.8(16) Å^{-3}; Molecules in Unit Cell, Z = 2; D_{calc}:1.42g.cm^{-3}; Crystal Dimensions (mm): 0.25 x 0.25 x 0.15; Temperature: 20°C.

3.4.3 Preparation of <u>4b</u> and <u>4c</u>

The completely halogen substituted [C$_5$H$_5$N]$^+$[<u>2</u>.Cu$_4$X$_5$]$^-$, <u>4b</u> (X=Br) and <u>4c</u> (X=I) were obtained by stirring the chloride derivative <u>4a</u> with an excess of the corresponding

potassium halide in CH_2Cl_2 (24h) followed by filtration and removal of solvent The products of **4b** and **4c** can be further purified by the crystallization procedure described above. Yield: bromide 88% ; iodide 90%.

4b: Anal. Calc for **4b** $C_{89}H_{74}Br_5Cu_4N_1O_8P_4$: C, 52.0; H, 3.6; N, 0.7. Found: C, 52.1; H, 3.9; N, 0.6. NMR in CH_2Cl_2: $\delta(^{31}P)$ = 133.0 [s, br]; $\delta(^1H)$ 2.74 [br, 16H, $C\underline{H}_2C\underline{H}_2Ph$], 4.86 [br, 4H, $C\underline{H}(CH_2)_2Ph$], 7.08 [t, $^4J_{PH}$ = 1.9Hz, 4H, Ar$\underline{H}$, ortho to O], 7.20-7.30 [m, 20H, $C_6\underline{H}_5$], 7.54 [s, 4H, Ar$\underline{H}$, meta to O], 7.52-7.63 [m, 12H, $PC_6\underline{H}_5$, para and meta to P], 8.02-8.12 [m, 8H, $PC_6\underline{H}_5$, ortho to P]. 8.28 [t, 2H, $C_5\underline{H}_5NH^+$, ortho to N], 7.67-7.80 [m, 3H, $C_5\underline{H}_5NH^+$, meta and para to N], 8.60 [s, br, 1H, $C_5H_5N.\underline{H}^+$]; IR: ν_{NH} = 3500cm^{-1} (w).

4c: Anal. Calc for **4c** $C_{89}H_{74}Cu_4I_5N_1O_8P_4$: C, 46.5; H, 3.3; N, 0.6. Found: C, 46.5; H, 3.2, N, 0.6. NMR in CD_2Cl_2: $\delta(^{31}P)$ = 122.6 [s, br]; $\delta(^1H)$ 2.73 [br, 16H, $C\underline{H}_2C\underline{H}_2Ph$], 4.86 [br, 4H, $C\underline{H}(CH_2)_2Ph$], 7.20 [t, $^4J_{PH}$ = 2.0Hz, 4H, Ar$\underline{H}$, ortho to O], 7.20-7.30 [m, 20H, $C_6\underline{H}_5$], 7.51 [s, 4H, Ar$\underline{H}$, meta to O], 7.52-7.66 [m, 12H, $PC_6\underline{H}_5$, para and meta to P], 8.05-8.15 [m, 8H, $PC_6\underline{H}_5$, ortho to P]. 8.28 [t, 2H, $C_5\underline{H}_5NH^+$, ortho to N], 7.67-7.77 [m, 3H, $C_5\underline{H}_5NH^+$, meta and para to N], 9.03 [s, br, 1H, $C_5H_5N.\underline{H}^+$); IR: ν_{NH} = 3500cm^{-1} (w).

3.4.4 Preparation of 4d:

Method 1: A mixture of excess of CuI (0.3g, 1.6mmol), pyridinium chloride (0.023g,

0.2mmol) and tetraphosphonito-calix[4]resorcinarene, **2**, (0.20g, 0.15mmol) in THF (20mL) were stirred at room temperature for one week. The excess CuI was removed by filtration. Colourless crystals can be obtained by diffusion of MeCN into the filtrate. The crystals were taken out , washed with MeCN (10mL) and dried under vacuum. A white solid, **4d**, was obtained. Yield: 0.26g, 81%.

Method 2: A mixture of n-Bu_4NI (0.2g, .55mmol) and **4a**, (0.20g, 0.11mmol) in CH_2Cl_2 was stirred at room temperature for one week. By using the same procedure as mentioned above, the white solid **4d** was obtained. Yield: 0.3g, 92%.

4d: Anal. Calc. for **4d**: $C_{89}H_{74}Cl_{1.75}Cu_4I_{3.25}N_1O_8P_4$, C, 50.0; H, 3.5. Found: C, 50.1; H, 3.6. NMR in CD_2Cl_2: $\delta(^{31}P)$ = 132.2 [br], 127.1 [br], 120.7 [br], assigned to PCu units with $PCu(\mu_4\text{-}I)Cl_2$, $PCu(\mu_4\text{-}I)ICl$ and $PCu(\mu_4\text{-}I)I_2$ coordination respectively; $\delta(^1H)$ 2.7 [br, 16H, $C\underline{H}_2C\underline{H}_2Ph$], 4.86 [br, 4H, $C\underline{H}(CH_2)_2Ph$], 7.08 [m, 4H, Ar<u>H</u>, ortho to O], 7.15-7.60 [m, 36H, $C_6\underline{H}_5$], 7.97-8.13 [m, 8H, $PC_6\underline{H}_5$, ortho to P]. 8.28 [t, 2H, $C_5\underline{H}_5NH^+$, ortho to N], 7.67-7.80 [m, 2H, $C_5\underline{H}_5NH^+$, meta and para to N], 5.35 [br, 1H, $C_5H_5N^+\underline{H}$]; IR: ν_{NH} = 3500cm^{-1} (w). FAB-M.S.: m/e = 2156.

3.4.5 Crystal Data of 4d

The crystals of **4d**, which were suitable for X-ray analysis were obtained by slow diffusion of MeCN (20mL) into a CH_2Cl_2 (2mL) solution of **4d** (150mg). The crystals lost solvent and became a powder when removed from the mother liquor. The crystals

were relatively stable for a short time when coated with paraffin oil. Hence a suitable colourless crystal of **4d** was wedged inside a capillary tube with mother liquor, flame sealed and transferred to an Enraf-Nonius CAD4 diffractometer for data collection at ambient temperature (23°C). Molecular Formula: $C_{89}H_{74}Cl_{1.75}Cu_4I_{3.25}N_1O_8P_4.2CH_3CN$, Formula Weight: 2220.2; Space group: triclinic, P-1, Cell dimensions: a = 17.830(3), b = 21.321(4), c = 13.779(4) Å, α = 103.3(2), β = 112.5(2), γ = 81.03(1)°, V = Å^3, Molecules in Unit Cell, Z = 2; D_{calc}:1.42g.cm^{-3}; Crystal Dimensions (mm): 0.25 x 0.25 x 0.15; Temperature: 20°C.

3.4.6 Preparation of 5a

A mixture of $[AgCCPh]_n$ (0.13g, 0.62mmol), pyridinium chloride (0.07g, 0.6mmol) and tetraphosphonito-calix[4]resorcinarene, **2**, (0.20g, 0.15mmol) in CH_2Cl_2 was stirred at room temperature for 15h to give a clear solution. By using the same procedure as described for the preparation of **4a**, a white solid **5a** was obtained. Yield: 0.25g, 83%. Anal. Calc for $C_{89}H_{74}Ag_4Cl_5N_1O_8P_4$ **5a**: C, 53.1; H, 3.7; N, 0.7 Found: C, 52.7; H, 4.0, N, 0.7. NMR in $CDCl_3$: $\delta(^{31}P)$ = 157.0 [2×d, $^1J_{Ag(109)-P}$ = 766.3Hz, $^1J_{Ag(107)-P}$ = 664.1Hz]; $\delta(^1H)$ 2.67 [br, 16H, C<u>H</u>$_2$C<u>H</u>$_2$Ph], 4.84 [br, 4H, C<u>H</u>(CH$_2$)$_2$Ph], 6.97 [t, $^4J_{PH}$ = 1.6Hz, 4H, Ar<u>H</u>, ortho to O], 7.15-7.32 [m, 20H, C$_6$<u>H</u>$_5$], 7.49 [s, 4H, Ar<u>H</u>, meta to O], 7.52-7.59(m, 12H, PC$_6$<u>H</u>$_5$, para and meta to P], 7.95-8.06 [m, 8H, PC$_6$<u>H</u>$_5$, ortho to P]. 8 18-8.30 [br, 2H, C$_5$<u>H</u>$_5$NH$^+$, ortho to N], 7.80-7.90 [br, 3H, C$_5$<u>H</u>$_5$NH$^+$, meta and para to N], 9.32 [s, br, 1H, C$_5$H$_5$N.<u>H</u>$^+$]. IR: ν_{NH} = 3500cm^{-1} (w).

3.4.7 Crystal Data for 5a

The crystals of 5a, which were suitable for X-ray analysis, were obtained by slow diffusion of MeCN (10mL) and EtCN (10mL) into a CH_2Cl_2 (2mL) solution of 4a (150mg). Difficulties were encountered in mounting a suitable data crystal. The crystals lost solvent when taken out of the mother liquor and became powder (even they were coated with paraffin oil). After a number of trials, a single crystal was wedged inside a Lindemann capillary tube along with a drop of mother liquor and the tube was flame sealed. Molecular Formula: $C_{88}H_{80}Ag_4Cl_5N_1O_8P_4.1.5C_2H_5CN.CH_2Cl_2$; Molecular weight: 2179.79; crystal system: triclinic; Space group: P1bar; Cell Dimensions: a = 15.532(4), b = 24.421(8), c = 14.049(8) Å, α = 90.98(4), β = 99.10(4), γ = 99.22(3)°; Cell volume: 5289(4) $Å^3$; Z = 2; Temperature: 23 °C; Density(calcd.): 1.395 $g.cm^{-3}$.

3.4.8 Preparation of 5b-5e

The completely halogen substituted complexes $[C_5H_6N]^+[2.Ag_4X_5]^-$, (X=Br, I) were obtained by stirring the chloride derivative 5a (0.2g, 0.1mmol) with an excess of the corresponding R_4NX (R = Me, X = Cl, 5b; R = n-Bu, X = I, 5c) or MX (M = Li, X = Br, 5d; M = Na, X = I, 5e) in CH_2Cl_2 for 24h. By using the same procedure described in preparation of 4b, products, 5c - 5e can be obtained. The products can be further purified by the crystallization procedure described above. Yield: 5b, 92%; 5c, 84%; 5d, 76% and 5e, 83%.

5b: Anal. Calc for **5b** $C_{88}H_{80}Ag_4Cl_5N_1O_8P_4$: C, 52.7; 4.0H, Found: C, 52.4; H, 3.7, NMR in $CDCl_3$: $\delta(^{31}P)$ = 155.6 [2×d, $^1J_{Ag(109)-P}$ = 745.2Hz, $^1J_{Ag(107)-P}$ = 645.4Hz]; $\delta(^1H)$ 3.30 [s, 16H, $(CH_3)_4N$], 2.64 [br, 16H, $C\underline{H}_2C\underline{H}_2Ph$], 4.82 [br, 4H, $C\underline{H}(CH_2)_2Ph$], 6.99 [t, $^4J_{PH}$ = 1.5Hz, 4H, Ar$\underline{H}$, ortho to O], 7.15-7.30 [m, 20H, $C_6\underline{H}_5$], 7.45 [s, 4H, Ar$\underline{H}$, meta to O], 7.52-7.60 [m, 12H, $PC_6\underline{H}_5$, para and meta to P], 7.95-8.05 [m, 8H, $PC_6\underline{H}_5$, ortho to P].

5c: Anal. Calc for **5c** $C_{100}H_{104}Ag_4I_5N_1O_8P_4$: C, 45.6; H, 4.0; N, 0.5. Found: C, 45.2; H, 3.9, N, 0.5. NMR in CD_2Cl_2: $\delta(^{31}P)$ = 138.6 [2×d, $^1J_{Ag(109)-P}$ = 507.0Hz, $^1J_{Ag(107)-P}$ = 439.5Hz]; $\delta(^1H)$ = 0.97 [t, $^3J_{HH}$ = 7.3Hz, 12H, $(C\underline{H}_3CH_2CH_2CH_2)_4N^+$], 1.40-1.55 [m, 8H, $(CH_3C\underline{H}_2CH_2CH_2)_4N^+$], 1.65 [br, 4H, $(CH_3CH_2C\underline{H}_2CH_2)_4N^+$)], 3.19 [t, $^3J_{HH}$= 8Hz, 4H, $(CH_3CH_2CH_2C\underline{H}_2)_4N^+$], 2.71 [br, 16H, $C\underline{H}_2C\underline{H}_2Ph$], 4.86 [br, 4H, $C\underline{H}(CH_2)_2Ph$], 7.19-7.28 [m, 24H, Ar$\underline{H}$, ortho to O and $C_6\underline{H}_5$], 7.45 [s, 4H, Ar$\underline{H}$, meta to O], 7.55-7.63 [m, 12H, $PC_6\underline{H}_5$, para and meta to P], 8.08-8.14 [m, 8H, $PC_6\underline{H}_5$, ortho to P].

5d: Anal. Calc for **5d** $C_{89}H_{74}Ag_4Br_5N_1O_8P_4$: C, 47.9; H, 3.3; Found: C, 47.4; H, 3.1. NMR in $CDCl_3$: $\delta(^{31}P)$ = 152.7 [2×d, $^1J_{Ag(109)-P}$ = 687.9Hz, $^1J_{Ag(107)-P}$ = 596.3Hz]; 2.69 [br, 16H, $C\underline{H}_2C\underline{H}_2Ph$], 4.84 [br, 4H, $C\underline{H}(C\underline{H}_2)_2Ph$], 7.05 [t, $^4J_{PH}$ = 1.6Hz, 4H, Ar$\underline{H}$, ortho to O], 7.15-7.31 [m, 20H, $C_6\underline{H}_5$], 7.47 [s, 4H, Ar$\underline{H}$, meta to O], 7.51-7.59 [m, 12H, $PC_6\underline{H}_5$, para and meta to P], 7.97-8.07 [m, 8H, $PC_6\underline{H}_5$, ortho to P]. 8.19-8.30 [br, 2H, $C_5\underline{H}_5NH^+$, ortho to N], 7.80-7.90 [br, 3H, $C_5\underline{H}_5NH^+$, meta and para to N], 9.31 [s, br, 1H, $C_5H_5N.\underline{H}^+$]; IR: ν_{NH} = 3500cm^{-1} (w).

5e: Anal. Calc for **5e** $C_{89}H_{74}Ag_4I_5N_1O_8P_4$: C, 43.2; H, 3.0; N, 0.6. Found: C, 43.5; H, 3.1, N, 0.6. NMR in $CDCl_3$: $\delta(^{31}P)$ = 141.2 (2×d, $^1J_{Ag(109)-P}$ = 551.6Hz, $^1J_{Ag(107)-P}$ = 486.8Hz); $\delta(^1H)$ 2.71(br, 16H, $C\underline{H}_2C\underline{H}_2Ph$), 4.84 (br, 4H, $C\underline{H}(CH_2)_2Ph$), 7.05(t, $^4J_{PH}$ = 1.6Hz, 4H, Ar<u>H</u>, ortho to O), 7.15-7.31(m, 20H, $C_6\underline{H}_5$), 7.47(s, 4H, Ar<u>H</u>, meta to O), 7.51-7.59(m, 12H, $PC_6\underline{H}_5$, para and meta to P), 7.97-8.07(m, 8H, $PC_6\underline{H}_5$, ortho to P). 8.19-8.30(br, 2H, $C_5\underline{H}_5NH^+$, ortho to N), 7.80-7.90(br, 3H, $C_5\underline{H}_5NH^+$, meta and para to N), 9.31(s, br, 1H, $C_5H_5N.\underline{H}^+$); IR: ν_{NH} = 3500cm^{-1} (w).

3.4.9 Preparation of 6:

A mixture of $AgNO_3$ (0.017g, 0.10mmol) in MeCN (5mL), and **5a**, (0.20g, 0.10mmol) in CH_2Cl_2 (5mL) was stirred at room temperature for 5h. The AgCl precipitate was removed by filtration. A yellowish solid can be obtained by diffusion of MeCN into the solution. Yield: 0.12g, 63%. Anal. Calc for **6** $C_{84}H_{68}Ag_4Cl_4P_4O_8$: C, 53.2; H, 3.6; Found: C, 52.9; H, 3.3. NMR in CD_2Cl_2: $\delta(^{31}P)$ = 161.7 [2×d, $^1J_{Ag(109)-P}$ = 820.7Hz, $^1J_{Ag(107)-P}$ = 711.4Hz]; $\delta(^1H)$ 2.69 [br, 16H, $C\underline{H}_2C\underline{H}_2Ph$], 4.80 [br, 4H, $C\underline{H}(CH_2)_2Ph$], 6.85 [t, ^4J_P = 1.5Hz, 4H, Ar<u>H</u>, ortho to O], 7.13-7.31 [m, 20H, $C_6\underline{H}_5$], 7.50 [s, 4H, Ar<u>H</u>, meta to O], 7.52-7.55 [m, 12H, $PC_6\underline{H}_5$, para and meta to P], 7.94-8.02 [m, 8H, $PC_6\underline{H}_5$, ortho to P].

3.4.10 Preparation of 7:

A mixture of Bu_4NI (0.041, 0.11mmol), and **6**, (0.20g, 0.11mmol) in CH_2Cl_2 (5mL) was stirred at room temperature for 0.5h. A white solid can be obtained by of diffusion

MeCN into the solution. Yield: 0.17g, 74%. Anal. Calc for 7 $C_{100}H_{104}Ag_4Cl_4I_1N_1O_8P_4$. C, 53.0; H, 4.6. Found: C, 52.7; H, 4.4. NMR in $CDCl_3$: $\delta(^{31}P)$ = 153.4 [2×d, $^1J_{Ag(109)-P}$ = 667.2Hz, $^1J_{Ag(107)-P}$ = 578.6Hz]; $\delta(^1H)$ 2.67 [br, 16H, $C\underline{H}_2C\underline{H}_2Ph$], 4.84 [br, 4H, $C\underline{H}(CH_2)_2Ph$], 6.97 [t, $^4J_{PH}$ = 1.6Hz, 4H, Ar$\underline{H}$, ortho to O], 7.15-7.32 [m, 20H, $C_6\underline{H}_5$], 7.49(s, 4H, Ar$\underline{H}$, meta to O], 7.52-7.59 [m, 12H, $PC_6\underline{H}_5$, para and meta to P], 7.95-8.06 [m, 8H, $PC_6\underline{H}_5$, ortho to P]. 8.18-8.30 [br, 2H, $C_5\underline{H}_5NH^+$, ortho to N], 7.80-7.90 [br, 3H, $C_5\underline{H}_5NH^+$, meta and para to N], 9.32 [s, br, 1H, $C_5H_5N.\underline{H}^+$].

3.4.11 Kinetic Studies of Halide Exchange of Alkyl Iodide and 5a

3.4.11.1 Measurement of Equilibrium Constant of [PPN]Cl and Me_2CHI Reaction in $CDCl_3$

Equal stoichiometric amounts of [PPN]Cl (0.0257g, 0.0612mmol) and Me_2CHI (6.1μL, 0.0611mmol) were dissolved in $CDCl_3$ (0.75mL) in an NMR tube. ^1H NMR spectra were recorded regularly until the integral ratio of Me_2CHCl to Me_2CHI did not change further (36h). The stoichiometric ratio of $[Me_2CHCl]/[Me_2CHI]$ was obtained by integration of the ^1H NMR resonances.

Equilibrium Constant:

$K = [Me_2CHCl][I^-]/[Me_2CHI][Cl^-]=([Me_2CHCl]^2/[Me_2CHI])^2 = 0.3$

Conversion: $\alpha = [Me_2CHCl]/([Me_2CHCl] + [Me_2CHI]) = 35.3\%$

Error Estimate: 5%

3.4.11.2 Kinetic Measurements of Halide Exchange between RI and 5a

General Experiment: 5a and Me_2CHI were dissolved in CD_2Cl_2. ^1H and ^{31}P NMR spectra

of the solution were recorded every 5 minutes. The stoichiometric ratios of [7]/[5a] and [RCl]/[RI] were obtained by resonances in both the ^{1}H and ^{31}P NMR spectra. Detailed experimental conditions are listed in Table 7

Table 7. Experimental conditions used in kinetic measurements

	5a	Temp.	RI	[Me_2CHI]	CD_2Cl_2
run 1	0.0163g	30°C	0.072mL (Me_2CHI)	0.90M	1g
run 2	0.0161g	30°C	0.050mL (Me_2CHI)	0.64M	1g
run 3	0.0165g	30°C	0.021mL (Me_2CHI)	0.28M	1g

Calculations:

For pseudo first order: $\ln[5a]^{\circ}/[5a] = \ln([7]/[5a] + 1) = kt$

For second order: $(1/[RI]^{\circ} - [5a]^{\circ})\ln\{1 + [7]/[5a]\}\{1/([RCl]/[RI] + 1)\} = kt$

$[RI]^{\circ} = [RCl] + [RI]$: initial concentration of alkyl halide

$[5a]^{\circ} = [7] + [5a]$: initial concentration of 5a

[5a] : concentration of 5a at time t

[7] : concentration of 7 at time t

[RCl]: concentration of RCl at time t

[RI]: concentration of [RI] at time t

x : concentration of 7 or Me_2CHCl

Error Estimated: 5%.

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Chapter Four

METAL CATION INCLUSION INDUCED BY ANION INCLUSION

4.1 INTRODUCTION

Since C. J. Pedersen discovered that macrocyclic polyethers can act as efficient ligands for alkali and alkaline earth metal cations, there has been much interest in macrocyclic ligands.[1] This type of study is of considerable interest in a number of areas such as ion storage and transport, the solvent extraction of metal cations, the synthesis of new chromatography materials and development of metal-ion selective reagents.[2] A further impetus to the study of such metal cation complexation comes from the recognition of the important roles of Na^+, K^+, Mg^{2+}, Ca^{2+} and Zn^{2+} ions in biological systems and Hg^{2+}, Cd^{2+} and Pb^{2+} ions in the environment.[3-6]

The most useful property of calixarenes is their ability to function as molecular baskets which can engulf small neutral or ionic guests into their cavities.[2-5] The complexing behaviour of calixarenes with alkali and alkaline earth cations has been examined extensively. Calixarenes possess ability to transport alkali cations only in strongly basic solution. The neutral calixarenes have low water solubility, but this is enhanced by deprotonation in basic solution and the resultant anions form neutral complexes with cations.[6,7] Therefore, in contrast to crown ethers which are more effective in neutral solution than in basic solution, calixarenes are more effective cation carriers in basic solution.[8-11] The cation selectivity of calixarenes is always towards the less hydrated Cs^+

It is believed that the transport is by an endo-calix complex.[12,13] The interactions between metal cations and calixarenes are considered to be essentially electrostatic. The calixarene derivatives with keto, ester and amide groups showed affinity for alkali cations in neutral conditions.[14,15] These calixarene derivatives are considered to be analogues of crown ethers.[15,16] Most of these cation receptors can only act as alkali or alkaline earth metal cation receptors with O or N donor atoms present or as transition metal cation receptors with N, P or S donor atoms present. To the best of my knowledge, no cation receptors which can bind both alkali or alkaline earth metal cations as well as transition metal cations have been reported. In this chapter, the first example of metal cation (both main group metals and transition metals) inclusion by a novel cation receptor with chlorine atoms as coordinating donors will be presented.

4.2 RESULTS AND DISCUSSIONS

In chapter 3, a tetradentate ligand **2** derived from a bowl-shaped calix[4]resorcinarene **1** by incorporation of four phosphonite donors has been used in the synthesis of the transition metal rimmed anion acceptors **3** (M = Cu) and **4** (M = Ag) as illustrated in Figure 1.

The unique selective anion inclusions of **3** and **4** and their structures have been discussed in Chapter 3. The space filling model of **3** and **4** indicated that the five chlorine atoms formed another small cup on the top of the calixresorcinarene bowl as illustrated in Figure 2. The Cl...Cl distances vary from ~3.7 - 4.2Å (Chapter 3, Table 4), giving a cavity which

could accommodate a metal ion with a diameter of ~2Å, if the chlorine covalently bonds to metal cations in the Cl_4 plane. The covalent bond radius of chlorine is 0.9Å,[17] and so the cavity is too small to encapsulate most metal cations, especially alkali cations which prefer to form ionic bonds. It is reasonable that the coordinating ability of the four chloride ligands arranged in a square will be enhanced by chelating effects and by the fifth chloride anion with its electrostatic attraction for cations. Can the chloride cup act as a cation receptor to hold or sandwich metal cations?

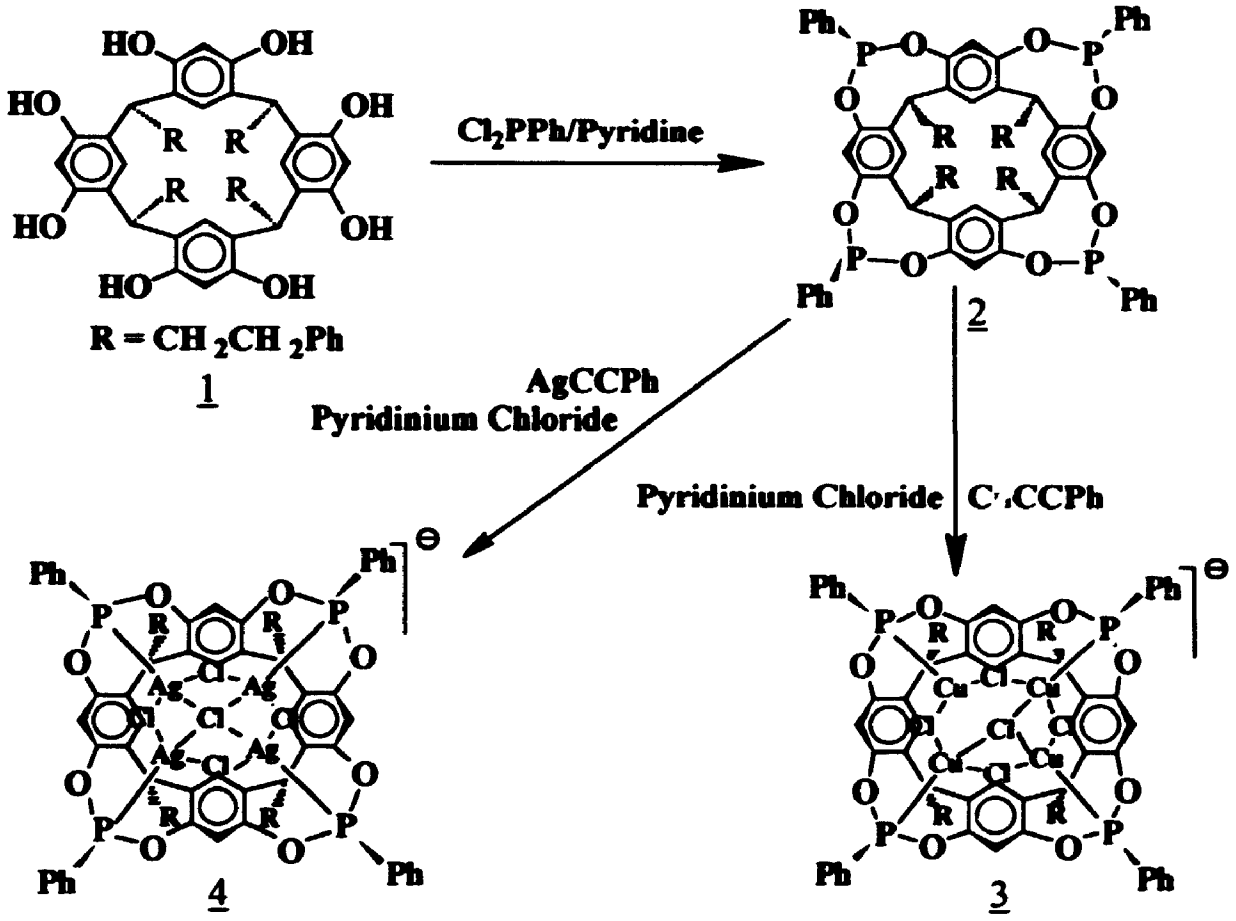


Figure 1. Preparation of transition metal rimmed anion acceptors 3 and 4

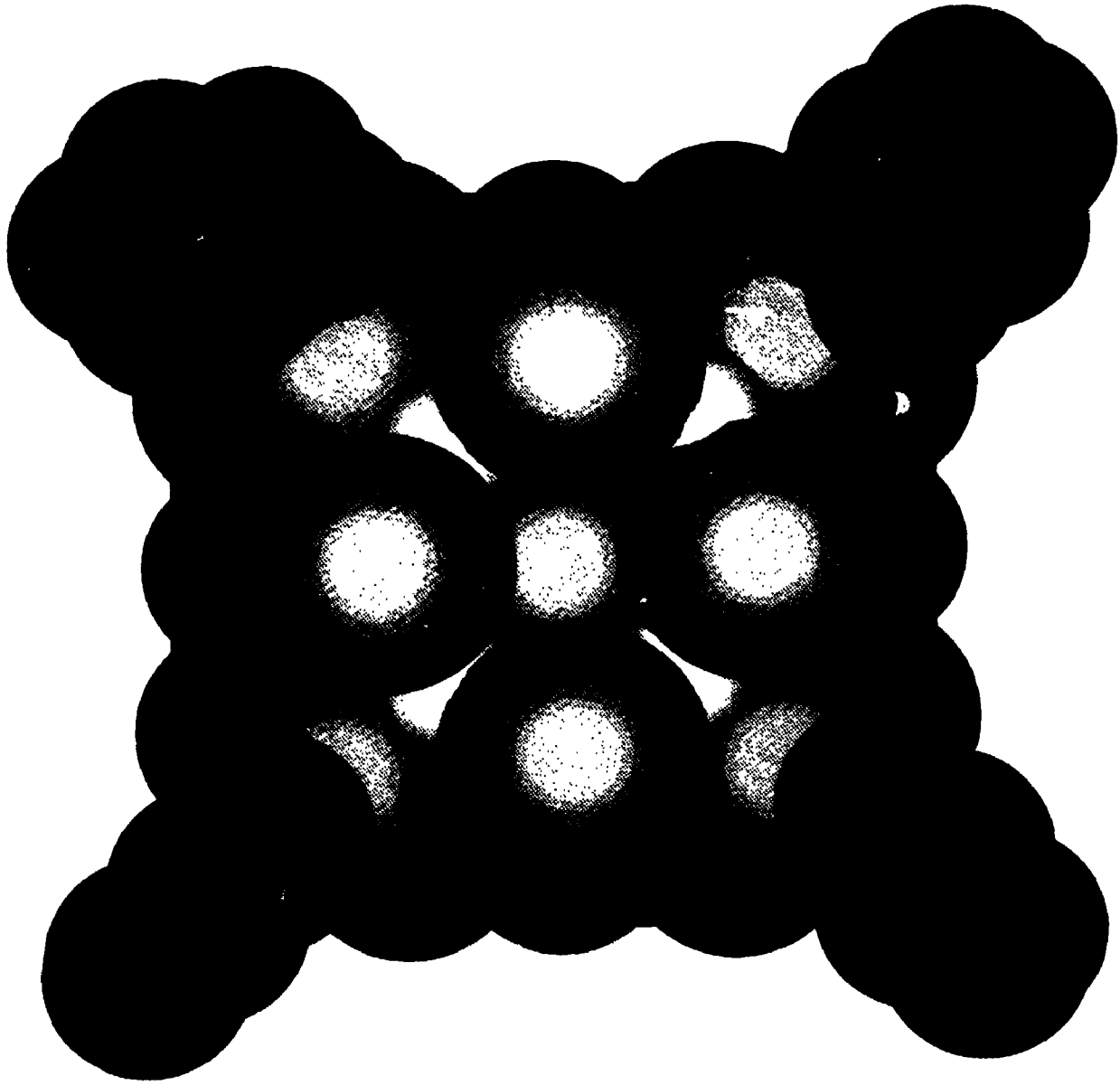


Figure 2 Space filling model of compound 3, showing the small cup formed by five chlorine atoms

4.2.1 Liquid-Liquid Metal Cation Extraction by Compounds 3 and 4

In order to test the ability of 3 and 4 to act as metal cation receptors, some preliminary studies on liquid-liquid extraction of several alkali and alkaline earth metal cations as well as transition metal cations have been carried out.[6] The results shown in Table 1 indicated that both 3 and 4 have the ability to extract these metal cations from aqueous solution into an organic medium. Interestingly, 4 has a strong affinity for Li^+, which is seldom extracted by other calixarene derivatives.[2, 5, 6,16] In this case, the Li^+ (van der Waals radius = 0.7Å) may be small enough to penetrate the small channel composed of four chlorine atoms and enter the cavity to bind to the occluded anion.

Table 1. Extraction of metal picrates from aqueous solution into CH_2Cl_2 at 25°C by 3 and 4

Ligand	Picrate Salt Extracted(%)					
	Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+
3	7.0	25.1	39.5	30.1	21.8	31.8
4	62.0	61.6	59.3	52.8	48.1	40.0
	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Pb^{2+}	Mn^{2+}
3	31.2	7.4	9.7	5.0	27.6	10.7
4	48.4	33.2	37.4	37.0	52.4	42.1
	Cd^{2+}	Ni^{2+}	Co^{2+}	Cu^{2+}	Zn^{2+}	
3	30.7	48.4	43.0	23.6	19.9	
4	59.0	37.1	47.0	81.2	40.1	

Aqueous phase: [metal chloride] = 0.1M; [metal picrates] = 8.3×10^{-5}M.
Organic phase: [ligand] = 8.3×10^{-5}M. No picrate extraction was observed in the absence of complexes 3 and 4.

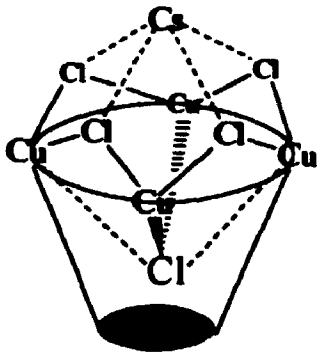
It is noted that due to the interference of the pyridinium cation present in the ligands 3 and 4 which may partially transfer into aqueous phase when the metal cation was

extracted into organic media, the values listed in Table 1 are relatively lower and have no absolute meaning. However, these data provide evidence for the complexation by 3 and 4 of metal cations in solution and show that 3 and 4 constitute a new class of cation receptor.

4.2.2 Formation and Structures of complexes of 3 or 4 with the Alkali Metal Cations

The alkali metal cation interaction with 3 or 4 could be quite different from alkali cation interactions with crown ethers, due to the different donor atoms and cavity sizes. It will be of interest to know if the metal cation extraction by 3 or 4 is driven by O...M or Cl...M (M = metal cation) interactions.

For investigating the structures of cation inclusion complexes, several such complexes have been synthesized and purified. Thus, treatment of a slurry of complex 3 or 4 at room temperature with excess alkali metal salts ($M = Na^+, K^+, Rb^+, Cs^+$) in acetone gave the corresponding alkali metal cation inclusion complexes 5 and 6 (see their Structures). The cation replacement was clearly indicated by the disappearance of pyridinium cation resonances which are present in the ^1H NMR spectrum of 3 or 4 as illustrated in Figure 3.



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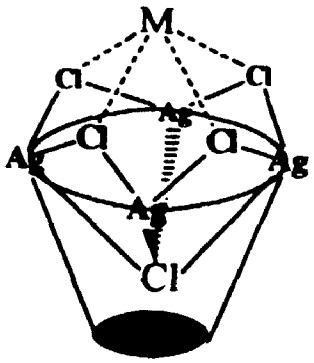


6 (6a, M = Cs; 6b, M = Rb
6c, M = K; 6d, M = Na)

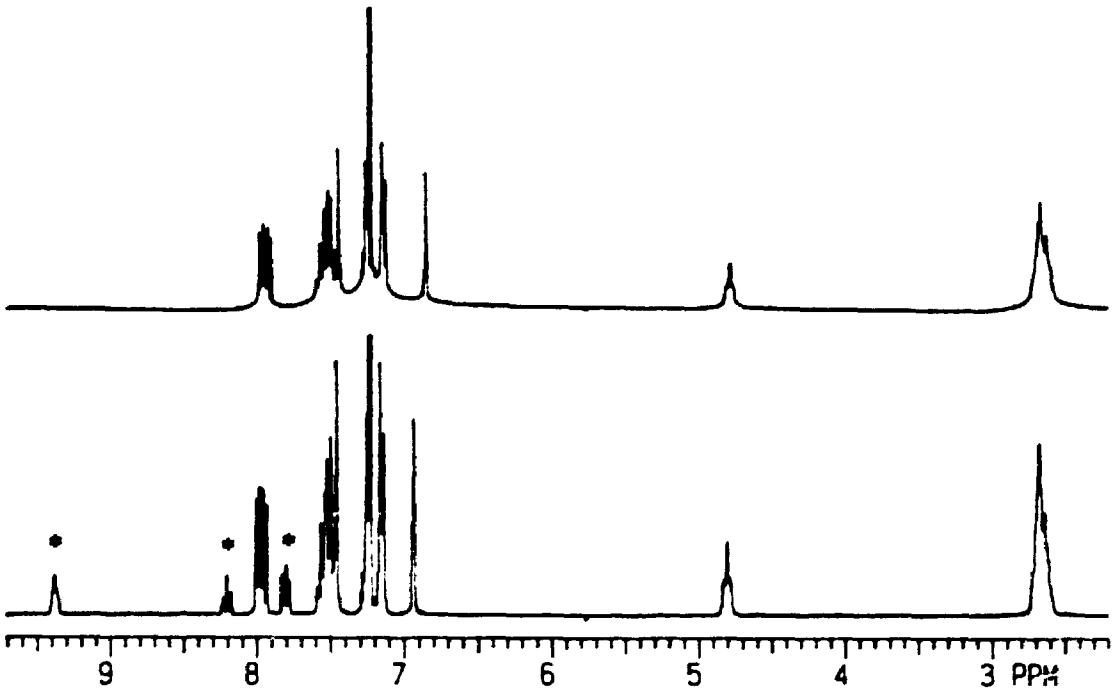


Figure 3. ^{1}H NMR spectra of compound 4 and cation complex 6a (notice the disappearance of pyridinium cation resonances which are marked with an asterisk in the lower spectrum)

Crystals of **5**, which were suitable for X-ray analysis, were obtained by recrystallization of **5** in $CDCl_3$ solution. The X-ray structure determination on the Cs^+ complex **5** revealed that each Cs^+ ion sits on the top of a chloride cup and two Cs^+ ions are sandwiched by two anions of **3** to give a 2:2 dimer. The structure of **5** is shown in Figure 4. The cesium atom appears in relatively close contact with the four chloride ligands of one anion of **3**, in which the interatomic distances Cl-Cs (mean 3.44(2)Å) are within experimental error of the typical ionic CsCl bond distance in CsCl (3.45Å).[18] Therefore the interactions between Cs^+...Cl are considered to be mainly electrostatic. The cesium cation also interacts more weakly with two chlorides from a second anion of **3** (mean Cl-Cs distance: 3.62(2)Å). A particularly interesting feature of the structure is that the cesium cation is also stabilized by π-interaction with a phenyl ring (mean Cs...C distance = 3.71(2)Å).[13] The shortest separation (3.59Å) is very close to the Cs-C distance of 3.53Å found for methyl cesium.[14] The interatomic distance of Cs^+ to occluded Cl^- (Cs...Cl(5) = 3.90Å) is too long to have any direct interactions. Thus the Cs^+ cation is encapsulated in a cage formed by six coordinated chloride ligands and one phenyl ring. It is reasonable to assume that the chloride-phenyl ring cage provides a particularly good environment for a Cs^+ ion after it has lost its hydration shell.[13] The Cs^+ ... Cs^+ separation in the sandwich arrangement is 4.24(1)Å, which is far enough to limit the charge repulsions and is also common in sandwich structures (4.5Å).[18]

By comparing the structural data for **3** and the cesium inclusion complex **5**, it is clear that the basic structural configuration of the calixresorcinarene bowl is unchanged and the metal cation coordination leads to a only slight enlargement of the cavity, as illustrated

in Table 2. However, the metal cation complexation does cause some significant changes. Thus, the occluded Cl^- in **5** only bridges between two opposite copper atoms (Cu(1)...Cl(5) = 2.55(1); Cu(3)...Cl(5) = 2.54(2); Cu(2)...Cl(5) = 2.72(2); Cu(4)...Cl(5) = 2.72(2)Å) rather than the μ_3-face bridged binding with three copper atoms found in compound **3**. As a result, the atoms Cu(1) and Cu(3) have irregular tetrahedral geometries with bond angles Cl-Cu-Cl and P-Cu-Cl in the ranges 95.1(6)-115.1(6)° and 111.8(6)-128.2(6)° while Cu(2) and Cu(4) have distorted trigonal planar geometry with bond angles Cl-Cu-Cl and P-Cu-Cl in the ranges 106.2(6)-120.1(6)° and 120.1(7)-119.4(6)° respectively. However, the ^{31}P NMR spectra of complex **5** in CD_2Cl_2 solution contain only one resonance either at room temperature or -70°C whereas in the solid state, according to the crystal structure, three such resonances would be expected if the dimeric structure **5** is retained in solution. This indicates that the Cs^+ complex dimer **5** becomes loosely sandwiched and is fluxional in solution, with the trapped μ_2-Cl^- migrating rapidly between the four copper atoms to give effective four-fold symmetry.

Table 2. Selected interatomic distances (Å) of **4a** and **5a**

	4a	**5**		**4a**	**5**
Cl(1)..Cl(2)	3.77(1)	3.77(2)	Cl(2)..Cl(3)	3.83(1)	3.80(2)
Cl(3)..Cl(4)	3.77(1)	3.79(2)	Cl(4)..Cl(1)	3.86(1)	3.86(2)
Cu(1)..Cu(2)	3.23(1)	3.42(2)	Cu(2)..Cu(3)	3.26(1)	3.45(2)
Cu(3)..Cu(4)	3.46(1)	3.37(2)	Cu(4)..Cu(1)	3.38(1)	3.35(2)
P(1)...P(2)	5.97(1)	6.10(2)	P(2)...P(3)	6.04(1)	5.97(2)
P(3)...P(4)	6.09(1)	6.18(2)	P(4)...P(1)	6.06(1)	6.07(2)
Cu(1)..Cl(5)	2.51(1)	2.55(1)	Cu(2)..Cl(5)	2.55(1)	2.79(1)
Cu(3)..Cl(5)	2.47(1)	2.54(1)	Cu(4)..Cl(5)	2.98(1)	2.72(1)

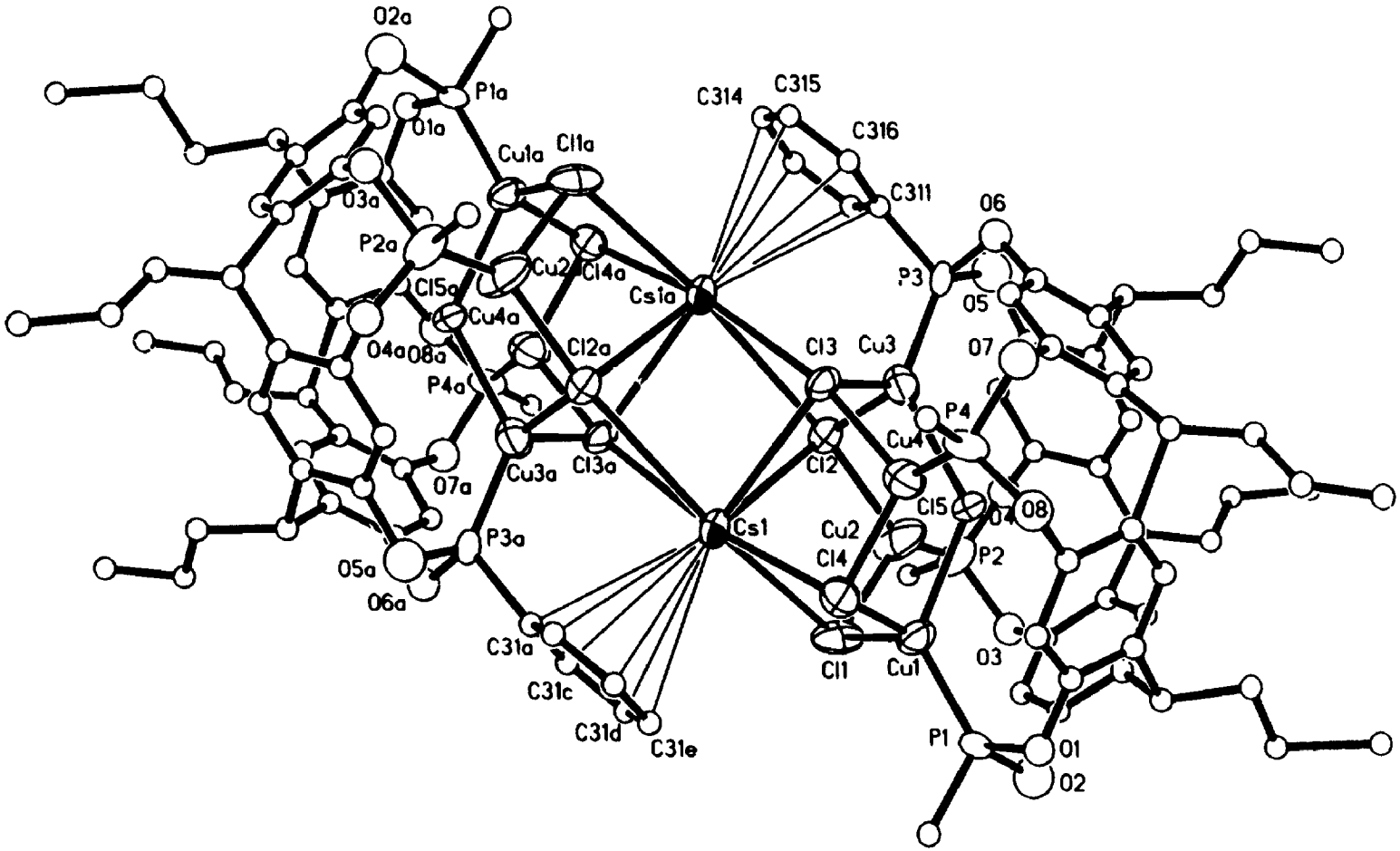


Figure 4. a). A side view of the molecular structure of **5** showing that the two caesium cations are sandwiched by two anionic bowl ligands. (The phenyl rings on $-CH_2CH_2Ph$ group, two uncoordinated phenyl rings on phosphorus atoms and all hydrogens have been omitted for clarity.)

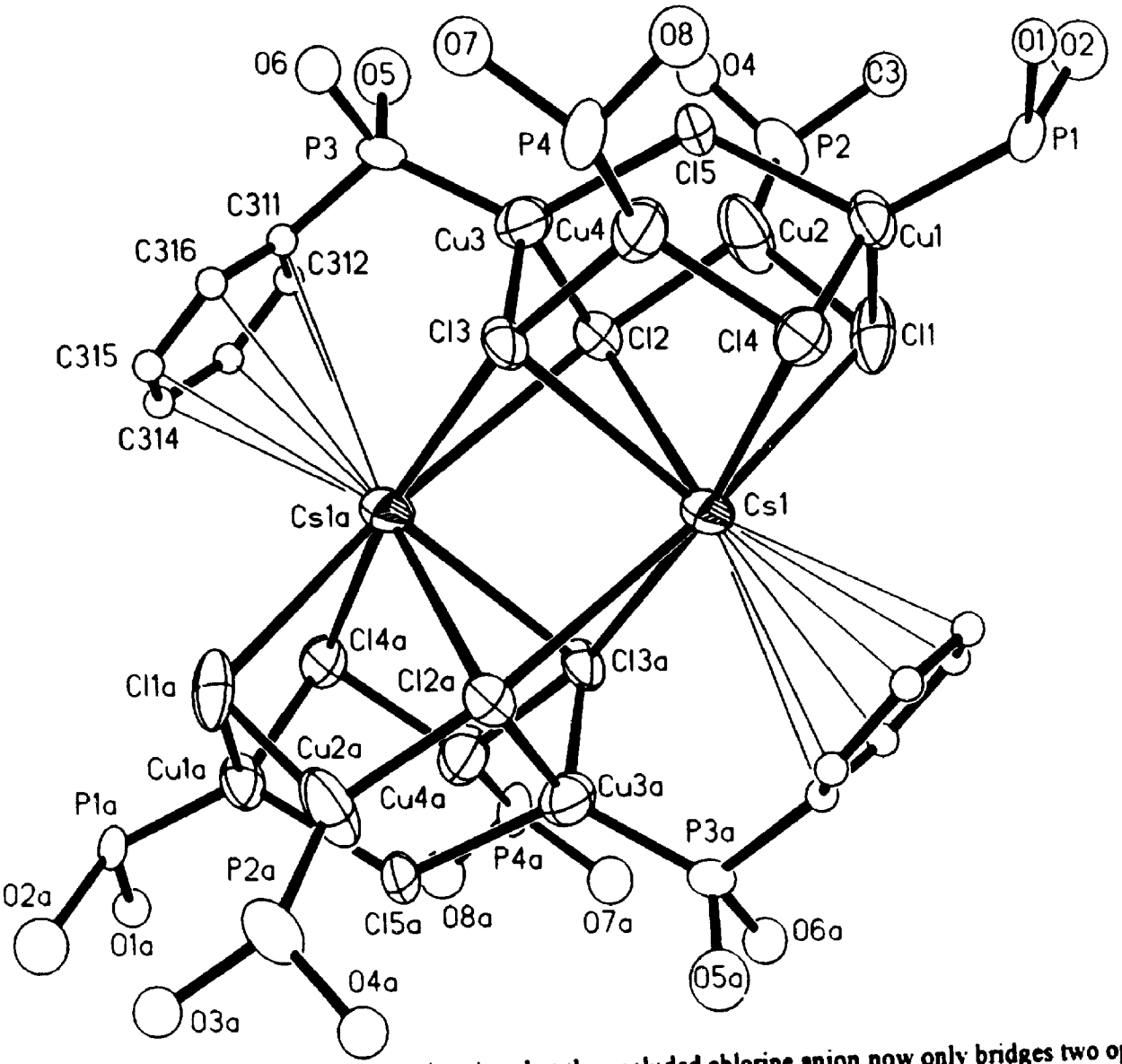


Figure 4. b). A side view of central part structure of 5 showing that the occluded chlorine anion now only bridges two opposite copper atoms

The ability to solubilize metal cations in media of low dielectric constant is necessary for many life processes.[19] The alkali metal cation complexes **5** and **6** have limited solubility in acetone but are appreciably soluble in CH_2Cl_2 and $CHCl_3$. It is interesting to question whether the observed solid state structure is retained in solution. The solution structures can be investigated by using NMR techniques. The complexation between compound **4** and alkali metal cations led to obvious chemical shift changes in the ^{31}P NMR spectra as shown in Figure 5. For the complexes with cations (K^+, Rb^+, Cs^+), their ^{31}P NMR spectra at room temperature and at -60°C remain the same. Therefore, it is deduced that the 2:2 dimer becomes more loosely bound in solution to allow a fluxional structure, although the alkali cations are still firmly bound to one bowl and there is no further dissociation. It is reasonable to assume that the structures of the alkali metal cation (M = K^+, Rb^+, Cs^+) complexes in solution are loosely bound but retain the same dimer configuration as that found for M = Cs^+ in the solid state.

Figure 5 shows that the resonances in the ^{31}P NMR spectrum of the Na^+ cation inclusion complex **6d** were broad at room temperature and so a low temperature (-70°C) ^{31}P NMR experiment was carried out. It showed there are two sets of doublets at low temperature corresponding to the Na^+ coordination complex **6d** and the free cation acceptor **4** as shown in Figure 6. It is quite possible that the Na^+ ion is too small to be sandwiched by two anions of **4** and that there is therefore a fast exchange in solution between the coordinated Na^+ complex and free ligand at room temperature.

When LiCl was treated with compound **4**, however, it gave a fairly complicated mixture,

represented by a ^{31}P NMR spectrum containing several resonances No pure Li^+ included complex is able to be separated. As discussed above for the Na^+ complex, the small Li^+ cation is not able to be sandwiched firmly by two anions of **3** and **4**. It is possible that it may enter the calixresorcinarene cavity, which is sealed by the four chlorine atoms, to combine with the anion. It seems clear that the anions of **3** and **4** prefer to sandwich relatively large and less hydrated alkali metal cations.

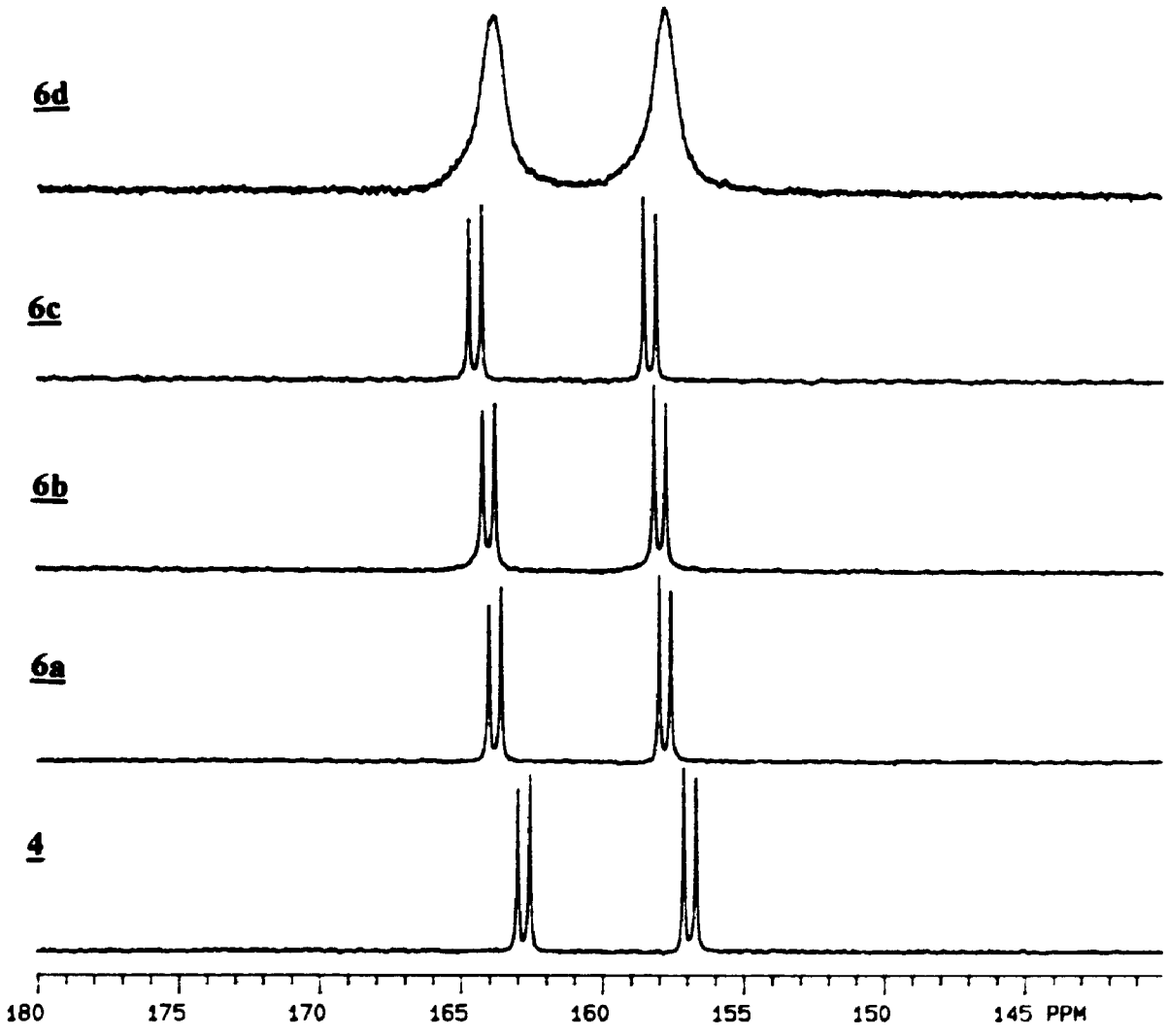


Figure 5. ^{31}P NMR spectra of compound **4** and cation complexes **6a** - **6d**

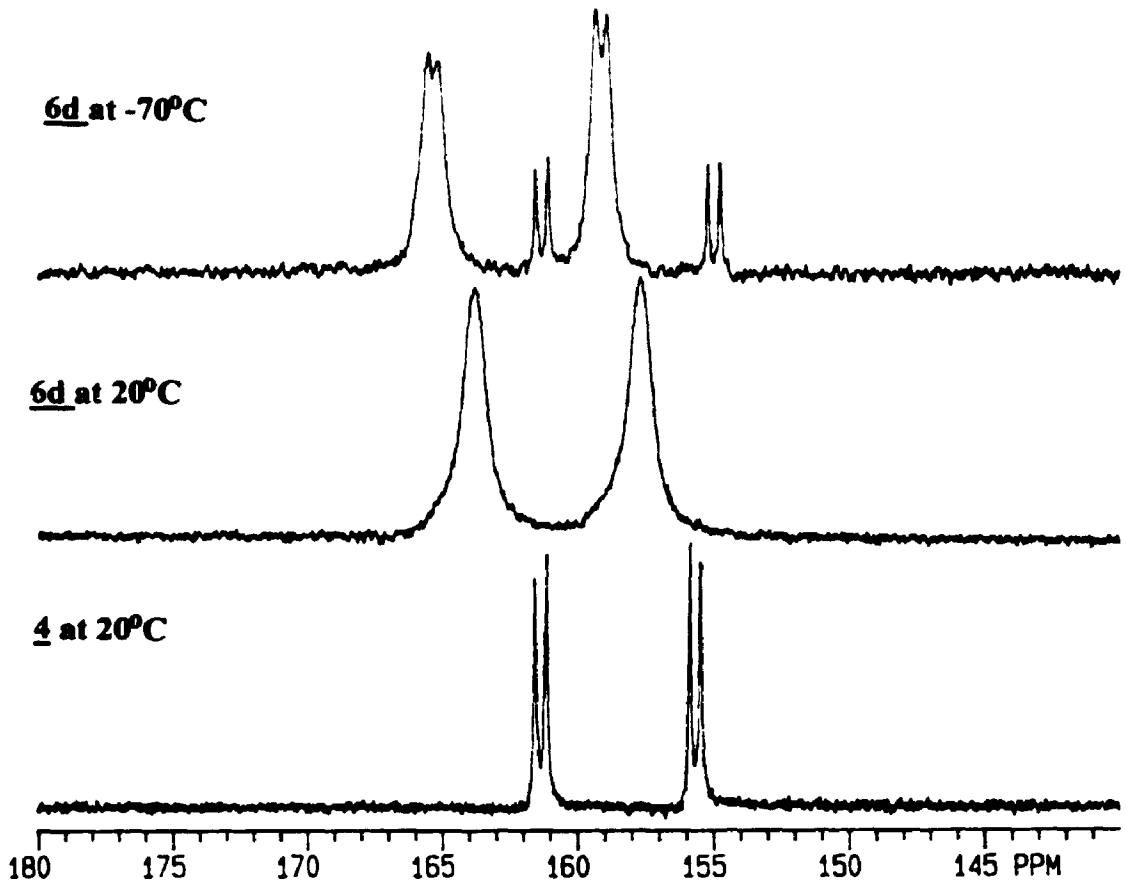


Figure 6. ^{31}P NMR spectra of (a) complex 4, (b) Na^+ complex 6d at room temperature and (c) Na^+ complex 6d at -70°C

It is interesting to note here that when compound 4 was treated with alkaline earth metal salts (M = Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+}) in acetone, no cation inclusion was observed. Since most common alkaline earth metal salts are quite insoluble in most organic solvents, it seems that some solubility of the metal salts in acetone is crucial if cation inclusion complexes are to be formed with 3 and 4. The ability of 3 and 4 to complex alkali metal cations selectively could provide a method for the separation of alkali metals from alkaline earth metals.

4.2.3 Formation and Structures of Complexes of 3 or 4 with Some Main Group Metal Cations

The compounds 3 and 4 showed affinity not only for alkali metal cations but also for some environmentally important main group metal cations. When the compound 3 or 4 was treated with a metal salt (M = Pb, Zn, Cd and Hg) having sufficient solubility in acetone, the metal cation was included to give complex 7 (3 Cd^{2+}) or 8 (4.M^{2+}, M = Zn, 8a; M = Cd, 8b; M = Hg, 8c; M = Pb, 8d).

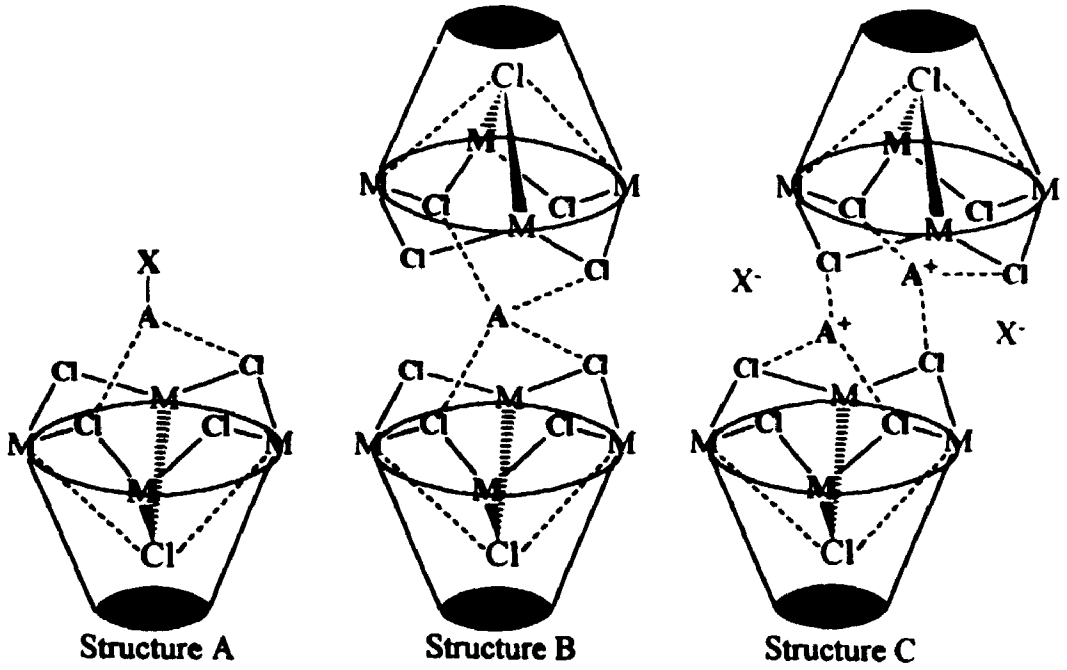
In contrast to the alkali metal cations whose complexes usually involve ionic bonding and so prefer a spherical charge distribution, there is usually a preferred coordination geometry for these main group metal cations. Therefore, the relative fit of the metal cation to the host's cavity and the preferred coordination geometry of the cation have great impact on the formation of the metal cation complex. Because the metal cations used here carry two positive charges, there are two general structures possible, in which the anion 3 or 4 replaces either one or two of the counter-anions associated with the metal cations to give structures A or B respectively, as illustrated in Figure 7. Since most of these cations are larger than the size of the cavity defined by the chloride ligands of 3 or 4, the 2:2 dimerization as illustrated in Structure C in which the M^{2+} ion bridges between two calixresorcinarene bowls is also possible.[20]

The ^1H NMR spectra of complexes 7 and 8 showed some chemical shifts changes and confirmed the disappearance of the pyridinium cation, but they did not provide much

information about the interactions of the metal cation with compounds **3** and **4**. Fortunately, ^{31}P NMR spectra do provide some structural information. In principle, the higher the coordination number at a Ag(I) centre, the lower the Ag-P coupling constant, ^{1}J(Ag-P) will be.[21] The chemical shifts and the coupling constants, $^{1}J(^{31}P\text{-}^{107}Ag)$ and $^{1}J(^{31}P\text{-}^{109}Ag)$, from the ^{31}P NMR spectra are listed in Table 3. Once the chloride ligands at the bowl rim coordinate with the metal cations, the four metal centers are pushed a little further apart and their interaction with the occluded anion to form the μ_4-face bridged bonding will be weakened. If the average coordination number of the silver ion decreases, the coupling constant between phosphorus and silver increases. According to this hypothesis, the stronger the coordination of **4** to the added metal ion, the larger the value of ^{1}J(Ag-P) should be. This is consistent with the larger coupling constant increase when the dipositive metal ions are coordinated with the anion of **4**, due to their stronger coordination compared to the alkali cations.

Table 3. ^{31}P NMR Chemical Shifts and Coupling Constants ^{1}J(Ag-P) in CD_2Cl_2

Metal cation complexes	$\delta(^{31}P)$ ppm	$^{1}J(^{109}Ag\text{-}^{31}P)$ Hz	$^{1}J(^{107}Ag\text{-}^{31}P)$ Hz
$[C_5H_5NH]$[Calixresorcinarene.$P_4Ag_4Cl_5$] **4**	157.0	766.3	664.1
Cs[Calixresorcinarene.$P_4Ag_4Cl_5$] **6a**	160.8	785.8	680.5
Rb[Calixresorcinarene.$P_4Ag_4Cl_5$] **6b**	160.4	783.1	679.0
K[Calixresorcinarene.$P_4Ag_4Cl_5$] **6c**	160.9	798.1	691.5
Zn[Calixresorcinarene.$P_4Ag_4Cl_5$]Cl **8a**	161.9	821.9	712.3
Cd[Calixresorcinarene.$P_4Ag_4Cl_5$]Cl **8b**	159.6	874.3	758.6
Hg[Calixresorcinarene.$P_4Ag_4Cl_5]_2$ **8c**	161.9	822.8	712.9
Pb[Calixresorcinarene.$P_4Ag_4Cl_5]_2$ **9**	162.1	820.7	712.2



7 (M = Cu, A = Cd, X = Cl); 8 (M = Ag: 8a, A = Hg, X = CN; 8b, A = Cd, X = Cl; 8c, A = Zn, X = Cl; 8d, A = Pb, X = Cl)

Figure 7. Some possible structures of metal cation complexes 7 and 8 (The geometry depicted for main group metals (A) may not be realistic in all cases due to the different geometric preferences of those metal ions)

As mentioned before, the main group metal ions M^{2+}, each has a preferred coordination geometry and so it will be of interest to discover what structural differences are found between alkali metal cation inclusion and other main group metal inclusion. The ^{31}P NMR spectrum of complex 7 or 8 in CD_2Cl_2 solution contains only one resonance and no coupling between the metal and phosphorus, $^2J(^{199}Hg\text{-}^{31}P)$, was observed in the complex 8c. These observations suggested that 7 and 8 still have C_4 symmetry and that the mercury binding is relatively weak. Although the microanalytical data of 7, 8a and 8b are in good agreement with structure A or C whereas the microanalytical data of 8c and 8d are in good agreement with structure B, the structures of complexes 7 or 8 are

difficult to predict. Spectroscopic studies were inconclusive in determining structures of the metal cation complexes, but an X-ray structure determination of the Hg^{2+} complex **8c** (Figure 8) revealed that Hg^{2+} ion also sits on the top of a chloride cup. The Hg^{2+} ion is sandwiched by two anions of **4** to give a 2:1 dimer. The bond distances and the angles are listed in Table 4. The mercury cation was found to be disordered in two positions as illustrated in Figure 8. It seems that the Hg^{2+} ion joins the two bowls together, but the two bowls are twisted to avoid steric hindrance caused by the phenyl rings on the upper rim of the calixresorcinarene bowl.

The mercury appears to be closely chelated by two opposite chloride ligands of one anion of **4**, in which the interatomic distances Cl(1)-Hg(1) = 2.64(2)Å and Cl(3) - Hg(1) = 2.69(2)Å. The mercury cation also interacts weakly with a third chloride ligand of the same anion of **4** [Cl(2)-Hg(1) distance: 2.93(2)Å] and much more strongly with another chloride ligand from the second anion of **4** [Cl(4a)-Hg(1) distance: 2.43(2)Å], thus pulling the mercury a little out of the chlorine cup. Therefore, the mercury is three coordinate with a coordination set of three coplanar chloride ligands [Cl(1), Cl(3) and Cl(4a)] but the mercury atom is displaced by 0.14(1)Å from this plane toward the Cl(2) ligand. The interatomic distances of Hg^{2+} to the occluded Cl^- [Hg...Cl(5) = 3.61(2)Å] and Hg^{2+} to the fourth chloride ligand [Cl(4)...Hg(1) = 3.41(2)Å] are too long for there to be any direct interactions. The set of four chloride ligands of the anion **4**, [Cl(1), Cl(2), Cl(3), Cl(4)], are coplanar to within 0.1571(5) Å; the mercury atom is displaced by 0.84Å from this plane away from the interior of the chloride cup. Thus the Hg^{2+} cation is half encapsulated in the cup formed by five chloride ligands.

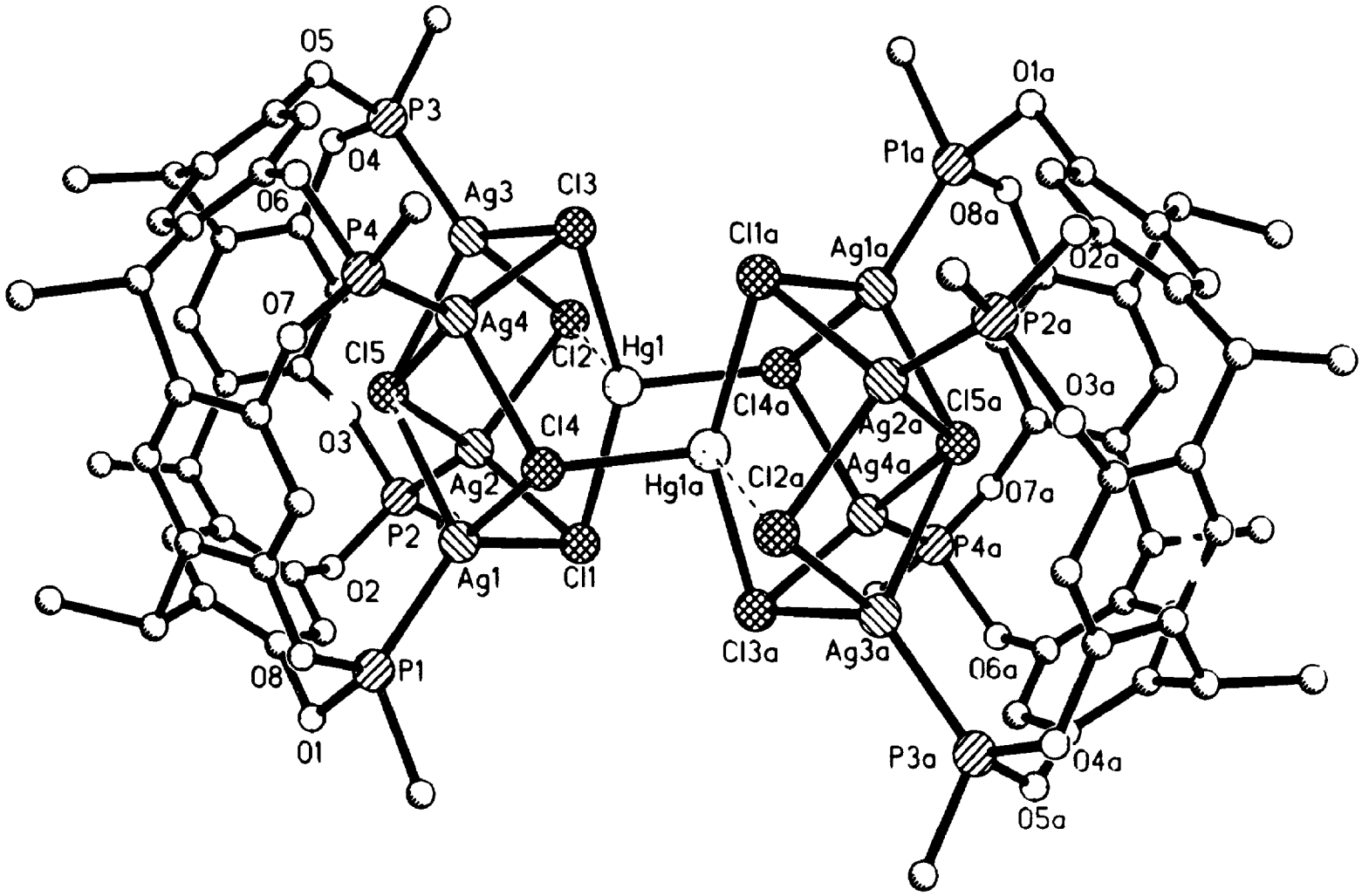


Figure 8. a). A side view of the molecular structure of **8c** showing that the one mercury cation is disordered in two positions and sandwiched by two anionic bowl ligands (The phenyl rings on the -CH_2CH_2Ph groups and on the phosphorus atoms and all hydrogens have been omitted for clarity.)

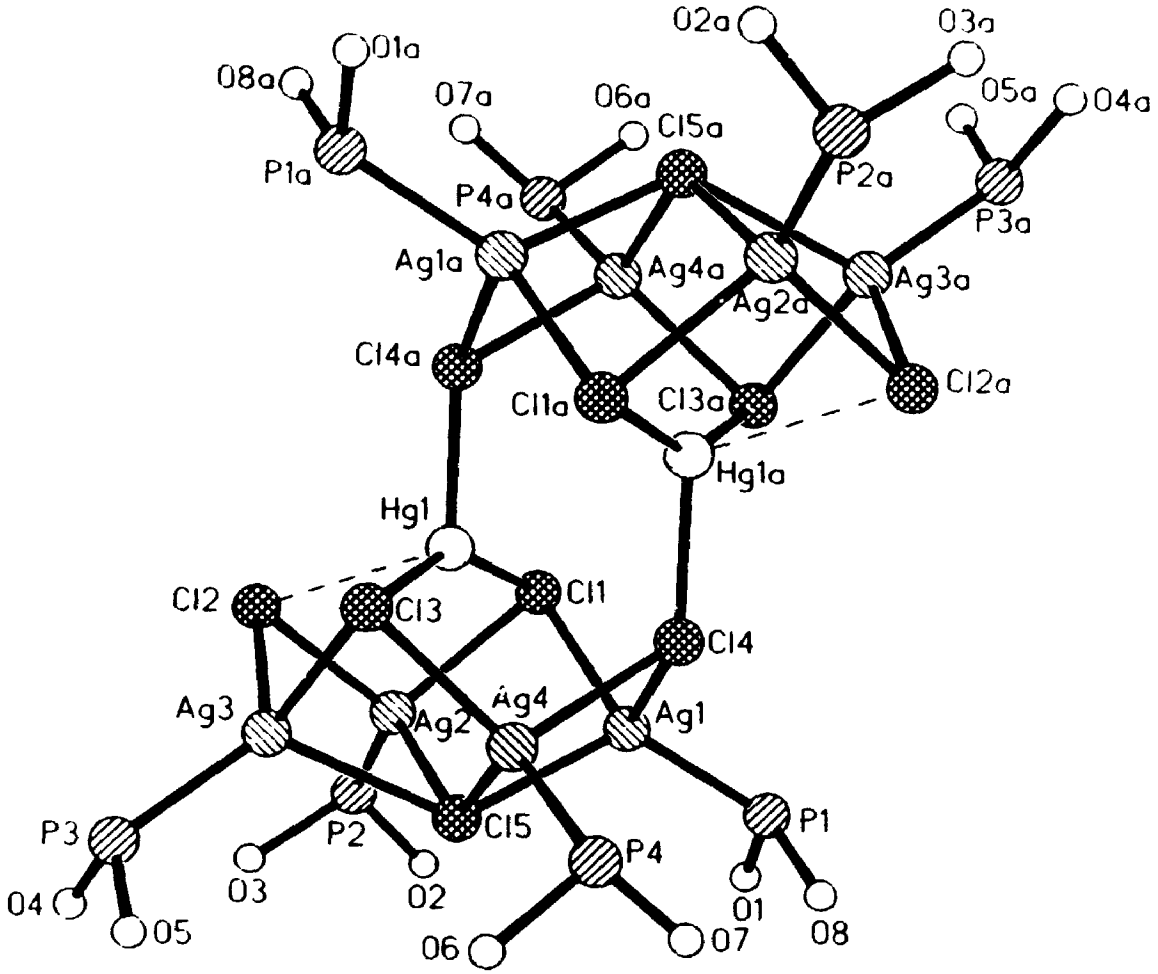


Figure 8. b). A side view of central part of the structure of **8c**, showing that the occluded chloride anion is still bridging between four silver atoms

Table 4. Selected bond lengths (Å) and angles (°) for **8c**.

(a) Interatomic distances (Å)

Hg(1)-Hg(1a)	3.704(7)	Hg(1)-Cl(4a)	2.43(2)	Hg(1)-Cl(3)	2.69(2)
Hg(1)-Cl(1)	2.64(2)	Hg(1)-Cl(2)	2.93(2)	Hg(1)-Ag(2)	3.407(8)
Hg(1)-Ag(3)	3.411(9)	Hg(1)-Cl(4)	3.41(2)	Hg(1)-Cl(5)	3.61(2)
Ag(1)-P(1)	2.36(2)	Ag(1)-Cl(1)	2.60(2)	Ag(1)-Cl(5)	2.69(2)
Ag(1)-Cl(4)	2.67(2)	Ag(2)-P(2)	2.39(2)	Ag(2)-Cl(1)	2.60(2)
Ag(2)-Cl(2)	2.59(2)	Ag(2)-Cl(5)	2.76(2)	Ag(2)-Ag(3)	3.543(8)
Ag(2)-Ag(4)	4.935(6)	Ag(3)-P(3)	2.36(2)	Ag(3)-Cl(3)	2.61(2)
Ag(3)-Cl(2)	2.61(2)	Ag(3)-Cl(5)	2.76(2)	Ag(3)-Ag(4)	3.412(8)
Ag(4)-P(4)	2.37(2)	Ag(4)-Cl(3)	2.55(2)	Ag(4)-Cl(4)	2.63(2)
Ag(4)-Cl(5)	2.73(2)	Cl(4)-Hg(1a)	2.43(2)		

(b) Selected bond angles (°)

Cl(4a)-Hg(1)-Cl(3)	94.7(6)	Cl(4a)-Hg(1)-Cl(1)	113.1(6)
Cl(3)-Hg(1)-Cl(1)	151.2(6)	Cl(4a)-Hg(1)-Cl(2)	113.8(7)
Cl(4a)-Hg(1)-Ag(2)	146.0(6)	Cl(3)-Hg(1)-Cl(4)	82.5(5)
Cl(1)-Hg(1)-Cl(4)	83.9(5)	Cl(2)-Hg(1)-Cl(4)	143.3(5)
P(1)-Ag(1)-Cl(1)	125.3(6)	P(1)-Ag(1)-Cl(5)	122.9(6)
Cl(1)-Ag(1)-Cl(5)	95.2(5)	P(1)-Ag(1)-Cl(4)	110.3(6)
Cl(1)-Ag(1)-Cl(4)	101.5(6)	Cl(5)-Ag(1)-Cl(4)	96.3(5)
P(2)-Ag(2)-Cl(1)	128.0(6)	P(2)-Ag(2)-Cl(2)	116.9(6)
Cl(1)-Ag(2)-Cl(2)	96.2(6)	P(2)-Ag(2)-Cl(5)	119.2(5)
Cl(1)-Ag(2)-Cl(5)	93.8(5)	Cl(2)-Ag(2)-Cl(5)	95.9(5)
P(3)-Ag(3)-Cl(3)	123.1(6)	P(3)-Ag(3)-Cl(2)	119.8(6)
Cl(3)-Ag(3)-Cl(2)	97.3(6)	P(3)-Ag(3)-Cl(5)	120.8(5)
Cl(3)-Ag(3)-Cl(5)	94.2(5)	Cl(2)-Ag(3)-Cl(5)	95.2(5)
P(4)-Ag(4)-Cl(3)	126.4(7)	P(4)-Ag(4)-Cl(4)	105.4(7)
Cl(3)-Ag(4)-Cl(4)	103.3(6)	P(4)-Ag(4)-Cl(5)	123.7(5)
Cl(3)-Ag(4)-Cl(5)	96.4(5)	Cl(4)-Ag(4)-Cl(5)	96.5(6)
Ag(2)-Cl(1)-Ag(1)	82.4(5)	Ag(2)-Cl(1)-Hg(1)	81.2(5)
Ag(1)-Cl(1)-Hg(1)	84.4(5)	Ag(2)-Cl(2)-Ag(3)	85.8(5)
Ag(4)-Cl(3)-Ag(3)	82.8(5)	Ag(4)-Cl(3)-Hg(1)	83.7(6)
Ag(3)-Cl(3)-Hg(1)	80.1(5)	Hg(1a)-Cl(4)-Ag(4)	116.2(8)
Hg(1a)-Cl(4)-Ag(1)	131.6(8)	Ag(4)-Cl(4)-Ag(1)	84.4(5)
Hg(1a)-Cl(4)-Hg(1)	77.6(6)	Ag(1)-Cl(5)-Ag(2)	77.9(4)
Ag(1)-Cl(5)-Ag(4)	82.1(4)	Ag(2)-Cl(5)-Ag(4)	128.3(5)
Ag(1)-Cl(5)-Ag(3)	129.1(5)	Ag(2)-Cl(5)-Ag(3)	79.9(4)
Ag(4)-Cl(5)-Ag(3)	76.8(4)		

For complexes 7, 8a and 8b, Zn^{2+} or Cd^{2+} may be too small (see Appendix 1) to be sandwiched by two anions of 3 or 4. These complexes might prefer structure A or structure C as illustrated in Figure 7.

The ^{31}P NMR spectra of complex 8c in CD_2Cl_2 solution contains only one resonance either at room temperature or at -70°C whereas in the solid state, according to the crystal structure, three such resonances would be expected. This indicates that the Hg^{2+} complex dimer 8c is fluxional in solution, with the trapped Hg^{2+} migrating rapidly between all the chloride ligands at the bowl rims to give effective four-fold symmetry.

4.3 CONCLUSION

The alkali metal cation complexes described in this chapter represent the first examples of sandwiched alkali metal cations in this new class of cation receptor and the first examples of alkali metal cation inclusion by chloride donor atoms. The novel anion acceptor proved to be a powerful cation receptor. The cation inclusion is driven by chelation by the four chloride ligands at the bowl rim and is enhanced by the presence of the occluded anion in the bowl cavity. The solubilities of both alkali and other main group metal salts are greatly enhanced when the metal cations are complexed by the cation acceptor 3 or 4. The ability of receptors to capture metal cations has potential applications in numerous areas such as the purification of alkali metal salts, environmental pollution control and metal cation recovery from contaminated cooling water containing radioactive ions, such as $^{137}Cs^{+}$ and $^{60}Co^{2+}$.

4.4 EXPERIMENTAL SECTION

Calixresorcinarene, 1 was prepared as described in the literature.[22] [Tetraphosphinitocalixresorcinarene], 2, $[C_5H_5NH]^+[Calixresorcinarene.P_4Cu_4Cl_4]^-$, 3, and $[C_5H_5N^+H][Calixresorcinarene.P_4Ag_4Cl_5]^-$, 4, were prepared as described in chapter 3 All the experiments were carried out under the conditions described in chapter 2. All the spectroscopic data were recorded by using the same instruments listed in Chapter 2. The crystal structures were solved by Dr. J. J. Vittal. Data were obtained by using an Enraf Nonius CAD4F diffractometer with graphite monochromator and MoKα radiation at λ = 0.71073 Å wavelength. UV-Vis measurements were recorded by using a Varian CARY 2290 spectrophotometer.

4.4.1 Cs[Calixresorcinarene.Cu_4Cl_5] 5

A slurry of $CsNO_3$ (0.1g, 0.51mmol) and $[C_5H_5N^+H][Calixresorcinarene.P_4Cu_4Cl_4]^-$, 3 (0.1g, 0.0545mmol) in acetone (20mL) was stirred at room temperature for 24 h. The slurry was filtered. The solid was washed with acetone (5mL×2) and dried under vacuum Then the solid was redissolved in CH_2Cl_2 (5mL) and the solution was filtered again to remove excess $CsNO_3$. The product was crystallized by diffusion of MeCN (10mL) into the filtrate. A white solid, which was washed with MeCN and dried under vacuum, was obtained. Yield: 0.085g, 78%. Anal. Calc for 5 $C_{84}H_{68}Cl_5Cs_1Cu_4O_8P_4$.2MeCN 1/2$Me_2CO$: C, 53.6; H, 3.9; Found: C, 53.7; H, 4.0%. NMR in CD_2Cl_2: $\delta(^{31}P)$ = 138 0 [s, br], $\delta(^1H)$ = 1.99 [s, 6H, C<u>H</u>$_3$CN], 2.13 [s, 3H, $(CH_3)_2CO$], 2.70 [br, 16H, C<u>H</u>$_2$C<u>H</u>$_2$Ph], 4 81

[br, 4H, C<u>H</u>$(CH_2)_2$Ph], 6.94 [s, 4H, Ar<u>H</u>, ortho to O), 7.18-7.29(m, 20H, C_6<u>H_5</u>], 7.50 [s, 4H, Ar<u>H</u>, meta to O], 7.51-7.60 [m, 12H, PC_6<u>H_5</u>, para and meta to P], 8.00-8.07 [m, 8H, PC_6<u>H_5</u>, ortho to P].

4.4.2 Crystal Data of Cs[Calixresorcinarene.$P_4Cu_4Cl_5$], <u>5</u>

The crystals of <u>5</u>, suitable for X-ray analysis, were obtained by slow diffusion of MeCN (10mL), EtCN (5mL) and n-PrCN (5mL) into a solution of <u>5</u> (50mg) in CH_2Cl_2 (2mL). The interatomic distances and angles are listed in Table 5. Since the structure refinement is incomplete, the results listed in Table 5 are preliminary and detailed crystal data are unavailable.

4.4.3 Cs[Calixresorcinarene.$P_4Ag_4Cl_5$], <u>6a</u>

A slurry of $CsNO_3$ (0.1g, 0.51mmol) and [$C_5H_5N^+$H][Calixresorcinarene.$P_4Ag_4Cl_5$]$^-$, <u>4</u> (0.1g, 0.0545mmol) in acetone (20mL) was stirred at room temperature for 24 h. By using the same procedure as described before, a white solid, which was washed with MeCN and dried under vacuum, was obtained. Yield: 0.090g, 79.7%. Anal. Calc for <u>6a</u> $C_{84}H_{68}Ag_4Cl_5Cs_1O_8P_4$: C, 48.7; H, 3.3; Found: C, 48.3; H, 3.2%. NMR in CD_2Cl_2: $\delta(^{31}P)$ = 160.8 [2×d, $^1J(^{109}Ag\text{-}^{31}P)$ = 785.8Hz, $^1J(^{107}Ag\text{-}^{31}P)$ = 680.5Hz]; $\delta(^1H)$ = 2.69 [br, 16H, C<u>H_2</u>C<u>H_2</u>Ph], 4.81 [br, 4H, C<u>H</u>$(CH_2)_2$Ph], 6.88 [s, 4H, Ar<u>H</u>, ortho to O], 7.14-7.32 [m, 20H, C_6<u>H_5</u>], 7.47 [s, 4H, Ar<u>H</u>, meta to O], 7.50-7.61 [m, 12H, PC_6<u>H_5</u>, para and meta to P], 7.94-8.01 [m, 8H, PC_6<u>H_5</u>, ortho to P].

Table 5. Selected bond lengths (Å) and angles (°) for **5**.

(a) Interatomic distances (Å)

Cs(1)-Cl(1)	3.37(2)	Cs(1)-Cl(4)	3.43(2)	Cs(1)-Cl(2)	3.46(2)
Cs(1)-Cl(3)	3.50(2)	Cs(1)-Cl(3a)	3.51(2)	Cs(1)-C(31e)	3.65(8)
Cs(1)-C(31f)	3.59(14)	Cs(1)-C(314)	3.81(4)	Cs(1)-C(311a)	3.70(5)
Cs(1)-Cl(2)	3.72(2)	Cs(1)-C(313)	3.92(11)	Cs(1)-C(312)	3.9(2)
Cu(1)-P(1)	2.16(2)	Cu(1)-Cl(4)	2.38(2)	Cu(1)-Cl(1)	2.41(2)
Cu(2)-P(2)	2.13(2)	Cu(2)-Cl(2)	2.37(2)	Cu(2)-Cl(1)	2.34(2)
Cu(2)-Cu(3)	3.348(12)	Cu(2)-Cu(4)	4.971(13)	Cu(3)-P(3)	2.17(2)
Cu(3)-Cl(2)	2.42(2)	Cu(3)-Cl(3)	2.41(2)	Cu(3)-Cu(4)	3.368(12)
Cu(3)-Cs(1)	4.015(9)	Cu(4)-P(4)	2.20(2)	Cu(4)-Cl(4)	2.35(2)
Cu(4)-Cl(3)	2.35(2)	Cl(2)-Cs(1a)	3.72(2)	Cl(3)-Cs(1a)	3.51(2)

(b) Selected bond angles (°)

Cl(1)-Cs(1)-Cl(4)	69.1(4)	Cl(1)-Cs(1)-Cl(2)	66.9(3)
Cl(4)-Cs(1)-Cl(3)	66.4(3)	Cl(2)-Cs(1)-Cl(3)	66.1(4)
Cl(2)-Cs(1)-Cl(3a)	74.8(4)	Cl(1)-Cs(1)-C(315a)	77(5)
Cl(3a)-Cs(1)-C(315a)	97(5)	Cl(1)-Cs(1)-C(316a)	95(5)
Cl(3a)-Cs(1)-C(316a)	77(5)	C(315a)-Cs(1)-C(316a)	22.1(6)
Cl(1)-Cs(1)-C(314a)	80(5)	Cl(3a)-Cs(1)-C(314a)	115(5)
C(315a)-Cs(1)-C(314a)	21.3(2)	Cl(1)-Cs(1)-C(311a)	114.9(8)
Cl(3a)-Cs(1)-C(311a)	75.8(8)	C(314a)-Cs(1)-C(311a)	43(5)
Cl(3)-Cs(1)-Cl(2a)	71.8(3)	Cl(3a)-Cs(1)-Cl(2a)	63.2(4)
C(314a)-Cs(1)-Cl(2a)	106(5)	Cl(1)-Cs(1)-C(313a)	99(5)
Cl(3a)-Cs(1)-C(313a)	112(5)	C(315a)-Cs(1)-C(313a)	36.9(7)
Cl(2a)-Cs(1)-C(313a)	87(5)	Cl(1)-Cs(1)-C(312a)	116(4)
Cl(3a)-Cs(1)-C(312a)	94(5)	C(315a)-Cs(1)-C(312a)	43.3(12)
Cl(2a)-Cs(1)-C(312a)	70(4)	C(313a)-Cs(1)-C(312a)	20.5(6)
Cu(2)-Cl(1)-Cs(1)	93.6(5)	Cu(1)-Cl(1)-Cs(1)	89.9(5)
Cs(1)-Cl(1)-Cl(5)	82.4(4)	Cs(1)-Cl(1)-Cl(2)	57.7(3)
Cs(1)-Cl(1)-Cl(4)	56.1(3)	Cs(1)-Cl(1)-Cl(3)	39.7(2)
Cu(2)-Cl(2)-Cs(1)	90.8(5)	Cu(3)-Cl(2)-Cs(1)	91.7(5)
Cs(1)-Cl(2)-Cl(5)	80.6(4)	Cu(3)-Cl(2)-Cl(1)	98.2(5)

4.4.4 Rb[Calixresorcinarene.$P_4Ag_4Cl_5$], 6b

A slurry of RbCl (0.1g, 1.17mmol) and [$C_5H_5N^+H$][Calixresorcinarene.$P_4Ag_4Cl_5$]$^-$, 4 (0.1g, 0.0545mmol) in acetone (20mL) was stirred at room temperature for 24 h. By using the same procedure as described before, a white solid, which was washed with MeCN and dried under vacuum, was obtained. Yield: 0.070g, 61.5%. Anal. Calc for 6b $C_{84}H_{68}Cl_5Ag_4O_8P_4Rb_1.3H_2O$: C, 48.9; H, 3.5; Found: C, 48.5; H, 3.4%. NMR in CD_2Cl_2: $\delta(^{31}P)$ = 160.4 [2×d, $^1J(^{109}Ag\text{-}^{31}P)$ = 783.1Hz, $^1J(^{107}Ag\text{-}^{31}P)$ = 679.0Hz]; $\delta(^1H)$ = 1.70 [s, br, 6H, H_2O], 2.73 [br, 16H, CH_2CH_2Ph], 4.84 [br, 4H, $CH(CH_2)_2Ph$], 6.84 [s, 4H, ArH, ortho to O], 7.16-7.28 [m, 20H, C_6H_5], 7.50 [s, 4H, ArH, meta to O], 7.54-7.62 [m, 12H, PC_6H_5, para and meta to P], 7.96-8.05 [m, 8H, PC_6H_5, ortho to P].

4.4.5 K[Calixresorcinarene.$P_4Ag_4Cl_5$], 6c

A slurry of KPF_6 (0.1g, 1.17mmol) and [$C_5H_5N^+H$][Calixresorcinarene.$P_4Ag_4Cl_5$]$^-$, 4 (0.1g, 0.0545mmol) in acetone (20mL) was stirred at room temperature for 24 h. By using the same procedure as described before, a white solid, which was washed with MeCN and dried under vacuum, was obtained. Yield: 0.084g, 76.1%. Anal. Calc for 6c $C_{84}H_{68}Ag_4Cl_5K_1O_8P_4.2H_2O$: C, 50.1; H, 3.6; Found: C, 49.8; H, 3.4%. NMR in CD_2Cl_2: $\delta(^{31}P)$ = 160.9 [2×d, $^1J(^{109}Ag\text{-}^{31}P)$ = 798.1Hz, $^1J(^{107}Ag\text{-}^{31}P)$ = 691.5Hz]; $\delta(^1H)$ = 1.70 [s, br, 4H, H_2O], 2.64 [br, 16H, CH_2CH_2Ph], 4.74 [br, 4H, $CH(CH_2)_2Ph$], 6.74 [s, 4H, ArH, ortho to O], 7.10-7.13 & 7.17-7.23 [m, 20H, C_6H_5], 7.48 [s, 4H, ArH, meta to O], 7.51-7.57 [m, 12H, PC_6H_5, para and meta to P], 7.87-7.93 [m, 8H, PC_6H_5, ortho to P].

4.4.6 Na[Calixresorcinarene.$P_4Ag_4Cl_5$], 6d

A slurry of $NaBPh_4$ (0.2g, 0.58mmol) and [$C_5H_5N^+H$][Calixresorcinarene $P_4Ag_4Cl_5$]$^-$, 4 (0.1g, 0.0545mmol) in acetone (20mL) was stirred at room temperature for 24 h. By using the same procedure as described before, a white solid, which was washed with MeCN and dried under vacuum, was obtained. Yield: 0.072g, 65.8%. Anal. Calc for 6d $C_{84}H_{68}Ag_4Cl_5Na_1O_8P_4.2H_2O$: C, 50.8; H, 3.6; Found: C, 50.3; H, 3.5%. NMR in CD_2Cl_2, 20C: $\delta(^{31}P)$ = 160.7 [d, br]; -70°C: $\delta(^{31}P)$ = 156.8 [2×d, $^1J(^{109}Ag\text{-}^{31}P)$ = 827.6Hz, $^1J(^{107}Ag\text{-}^{31}P)$ = 715.7Hz]; $\delta(^1H)$ = 1.75 [s, br, 4H, $\underline{H}_2O$], 2.72 [br, 16H, $C\underline{H}_2C\underline{H}_2Ph$], 4.82 [br, 4H, $C\underline{H}(CH_2)_2Ph$], 6.84 [s, 4H, Ar$\underline{H}$, ortho to O], 7.16-7.32 [m, 20H, $C_6\underline{H}_5$], 7.54 [s, 4H, Ar$\underline{H}$, meta to O], 7.55-7.65 [m, 12H, $PC_6\underline{H}_5$, para and meta to P], 7.94-8.02 [m, 8H, $PC_6\underline{H}_5$, ortho to P].

4.4.7 Cd[Calixresorcinarene.$P_4Cu_4Cl_5$]Cl, 7

A slurry of $CdCl_2$ (0.1g, 0.55mmol) and [$C_5H_5N^+H$][Calixresorcinarene.$P_4Cu_4Cl_5$]$^-$, 3 (0.1g, 0.0545mmol) in acetone (20mL) was stirred at room temperature for 24 h. The slurry was filtered. The solid was washed with acetone (5mL×2) and dried under vacuum. Then the solid was redissolved in CH_2Cl_2 (5mL) and the solution was filtered again to remove excess of $CdCl_2$. The product was crystallized by diffusion of MeCN (10mL) into the filtrate. A white solid, which was washed with MeCN and dried under vacuum, was obtained. Yield: 0.065g, 66%. Anal. Calc for 5 $C_{84}H_{68}CdCl_6Cu_4O_8P_4.(CH_3)_2CO$: C, 53.2; H, 3.8; Found: C, 53.5; H, 3.9%. NMR in CD_2Cl_2: $\delta(^{31}P)$ = 141.5 [s, br]; $\delta(^1H)$ =

2.16 [s, 3H, $(CH_3)_2CO$], 2.69 [br, 16H, $C\underline{H}_2C\underline{H}_2Ph$], 4.81 [br, 4H, $C\underline{H}(CH_2)_2Ph$], 6.82 [s, 4H, Ar$\underline{H}$, ortho to O), 7.16-7.29(m, 20H, $C_6\underline{H}_5$], 7.45 [s, 4H, Ar$\underline{H}$, meta to O], 7.52-7.62 [m, 12H, $PC_6\underline{H}_5$, para and meta to P], 7.92-8.05 [m, 8H, $PC_6\underline{H}_5$, ortho to P].

4.4.8 Zn[Calixresorcinarene.$P_4Ag_4Cl_5$]Cl, 8a

A slurry of $ZnCl_2$ (0.1g, 0.74mmol) and $[C_5H_5N^+H][Calixresorcinarene.P_4Ag_4Cl_5]^-$, **4** (0.1g, 0.0545mmol) in acetone (20mL) was stirred at room temperature for 24 h. By using the same procedure as described before, a white solid, which was washed with MeCN and dried under vacuum, was obtained. Yield: 0.072g, 69%. Anal. Calc for **8a** $C_{84}H_{68}Ag_4Cl_6O_8P_4Zn.MeCN$: C, 49.8; H, 3.5; Found: C, 49.7; H, 3.4%. NMR in $CDCl_3$: $\delta(^{31}P)$ = 161.9; [2×d, $^1J(^{109}Ag\text{-}^{31}P)$ = 821.9Hz, $^1J(^{107}Ag\text{-}^{31}P)$ = 712.3Hz]; $\delta(^1H)$ = 1.92 [s, 3H, $C\underline{H}_3CN$], 2.70 [br, 16H, $C\underline{H}_2C\underline{H}_2Ph$], 4.80 [br, 4H, $C\underline{H}(CH_2)_2Ph$], 6.86 [s, 4H, Ar$\underline{H}$, ortho to O], 7.11-7.33 [m, 20H, $C_6\underline{H}_5$], 7.48 [s, 4H, Ar$\underline{H}$, meta to O], 7.50-7.58 [m, 12H, $PC_6\underline{H}_5$, para and meta to P], 7.90-8.02 [m, 8H, $PC_6\underline{H}_5$, ortho to P].

4.4.9 Cd[Calixresorcinarene.$P_4Ag_4Cl_5$]Cl, 8b

A slurry of $CdCl_2$ (0.1g, 0.55mmol) and $[C_5H_5N^+H][Calixresorcinarene.P_4Ag_4Cl_5]^-$, **4** (0.1g, 0.0545mmol) in acetone (20mL) was stirred at room temperature for 24 h. By using the same procedure as described before, a white solid, which was washed with MeCN and dried under vacuum, was obtained. Yield: 0.044g, 41%. Anal. Calc for **8b** $C_{84}H_{68}Ag_4Cd_1Cl_6O_8P_4$: C, 48.5; H, 3.3; Found: C, 48.9; H, 3.5%. NMR in $CDCl_3$: $\delta(^{31}P)$

= 159.6 [2×d, $^1J(^{109}Ag\text{-}^{31}P)$ = 874.3Hz, $^1J(^{107}Ag\text{-}^{31}P)$ = 758.6Hz]; $\delta(^1H)$ = 2.68 [br, 16H, $C\underline{H}_2C\underline{H}_2Ph$], 4.79 [br, 4H, $C\underline{H}(CH_2)_2Ph$], 6.89 [s, 4H, Ar$\underline{H}$, ortho to O], 7.13-7.16 & 7.25-7.31 [m, 20H, $C_6\underline{H}_5$], 7.45 [s, 4H, Ar$\underline{H}$, meta to O], 7.46-7.59 [m, 12H, $PC_6\underline{H}_5$, para and meta to P], 7.84-7.98 [m, 8H, $PC_6\underline{H}_5$, ortho to P].

4.4.10 Hg[Calixresorcinarene.$P_4Ag_4Cl_5$]$_2$, 8c

A slurry of $Hg(CN)_2$ (0.2g, 0.79mmol) and $[C_5H_5N^+H][Calixresorcinarene.P_4Ag_4Cl_5]^-$, 4 (0.1g, 0.0545mmol) in acetone (20mL) was stirred at room temperature for 24 h. By using the same procedure as described before, a white solid, which was washed with MeCN and dried under vacuum, was obtained. Yield: 0.081g, 53.6%. Anal. Calc for 8c $C_{85}H_{68}Ag_4Cl_5Hg_1N_1O_8P_4$: C, 49.5; H, 3.4; Found: C, 49.8; H, 3.6%. NMR in $CDCl_3$: $\delta(^{31}P)$ = 161.9; [2×d, $^1J(^{109}Ag\text{-}^{31}P)$ = 822.8Hz, $^1J(^{109}Ag\text{-}^{31}P)$ = 712.9Hz]; $\delta(^1H)$ = 1.75 [s, br, 2H, $\underline{H}_2O$], 1.95 [s, 6H, $C\underline{H}_3CN$], 2.68 [br, 16H, $C\underline{H}_2C\underline{H}_2Ph$], 4.79 [br, 4H, $C\underline{H}(CH_2)_2Ph$], 6.84 [s, 4H, Ar$\underline{H}$, ortho to O], 7.13-7.17 & 7.24-7.29 [m, 20H, $C_6\underline{H}_5$], 7.48 [s, 4H, Ar$\underline{H}$, meta to O], 7.49-7.53 [m, 12H, $PC_6\underline{H}_5$, para and meta to P], 7.93-8.01 [m, 8H, $PC_6\underline{H}_5$, ortho to P].

4.4.11 Pb[Calixresorcinarene.$P_4Ag_4Cl_5$]$_2$, 8d

A slurry of $Pb(NO_3)_2$ (0.2g, 0.60mmol) and $[C_5H_5N^+H]$ [Calixresorcinarene.$P_4Ag_4Cl_5$]$^-$ 4 (0.1g, 0.0545mmol) in acetone (20mL) was stirred at room temperature for 24 h. By using the same procedure as described before, a white solid, which was washed with

MeCN and dried under vacuum, was obtained. Yield: 0.091g, 82%. Anal. Calc for **8d** $C_{168}H_{136}Ag_8Cl_{10}O_{16}P_8Pb_1$: C, 49.5; H, 3.4; Found: C, 49.8; H, 3.9%. NMR in $CDCl_3$: $\delta(^{31}P)$ = 162.1 [2×d, $^1J(^{109}Ag\text{-}^{31}P)$ = 820.7Hz, $^1J(^{109}Ag\text{-}^{31}P)$ = 712.2Hz]; $\delta(^1H)$ = 1.75 [s, br, 2H, $\underline{H}_2O$], 2.14 [s, 3H, $(CH_3)_2CO$], 2.69 [br, 16H, $C\underline{H}_2C\underline{H}_2Ph$], 4.78 [br, 4H, $C\underline{H}(CH_2)_2Ph$], 6.80 [s, 4H, Ar$\underline{H}$, ortho to O], 7.14-7.18 & 7.24-7.29 [m, 20H, $C_6\underline{H}_5$], 7.48 [s, 4H, Ar$\underline{H}$, meta to O], 7.51-7.52 [m, 12H, $PC_6\underline{H}_5$, para and meta to P], 7.94-7.98 [m, 8H, $PC_6\underline{H}_5$, ortho to P].

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Chapter Five

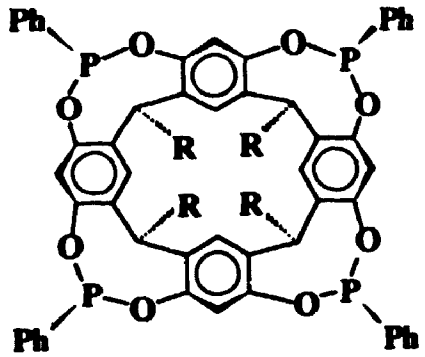
METAL CATION ACCEPTORS: SULPHIDE AND SELENIDE DERIVATIVES OF A PHOSPHONITO-CALIXRESORCINARENE

5.1 INTRODUCTION

As mentioned in chapter 4, there has been much interest in macrocyclic ligands for use as selective metal ion complexing reagents. In principle, it is possible to discriminate between closely related metal ions based on their relative fit for the cavity of the host ligand, although the selectivity could be influenced by several other factors such as the coordinating atoms, the solvent and the conformation of host.

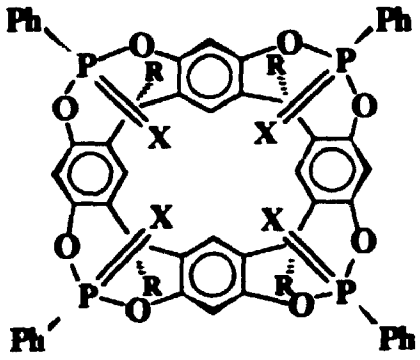
In chapter 2, the synthesis of the phosphonito-cavitand, 1 was presented. Although 1 has notable coordination ability, it is unstable in the presence of a microscopic amount of water and so it is not possible to carry out a study of its inclusion chemistry. As far as its stereochemistry is concerned, 1, which has a bowl shaped architecture with all phenyl groups on phosphorus directed outwards and all lone pair electrons on phosphorus inwards, is too open on the upper rim to imprison small guests. Since all the lone pairs electrons on phosphorus are directed to the middle of the bowl, any coordination by or oxidation of the phosphorus(III) atoms will cover the bowl to form a sealed cavity which could imprison a small guest. In chapter 3, it has been shown that a set of transition metal atoms on the upper rim of calixresorcinarenes, formed by coordination with the phosphorus(III) atoms, is able to close the bowl and to capture an anion in its cavity In

this chapter, the preparation of sulphide and selenide derivatives of the phosphonito-cavitands **2** (X = S, **2a**; X = Se, **2b**) by oxidation of **1** will be reported. The compounds, **2a** and **2b** appear to be versatile hosts for either neutral solvents or metal cations as guests.



R = CH_2CH_2Ph

1



R = CH_2CH_2Ph

2 (2a, X = S; **2b**, X = Se)

5.2 RESULTS AND DISCUSSION

5.2.1 Oxidation of the Phosphorus Atoms of 3

The sulphide and selenide derivatives **2a** and **2b** can be prepared by direct oxidation of **1** with S or Se. Thus, treatment of **1** with S or Se in CH_2Cl_2 gave an air and moisture stable product **2**. The large chemical shift changes [$\delta(^{31}P)$ = 166 for **1**, $\delta(^{31}P)$ = 81 for **2a**, and $\delta(^{31}P)$ = 87 for **2b**] and clear ^{77}Se satellites [$^1J(^{77}Se\text{-}^{31}P)$ = 473Hz] in the ^{31}P NMR spectrum of **2b** indicated that the P(III) atoms in **1** have been oxidized to P(V). The single resonance observed in the ^{31}P NMR spectrum of each complex **2** in CD_2Cl_2 suggested that the complex **2** has C_4 symmetry in solution. Therefore **2** is expected to have a similar cone conformation as **1**, but with the four X (X = S or Se) groups on

phosphorus pointing to the centre of the calixresorcinarene bowl. The space filling model clearly showed that the four X (X = S, Se) groups capped the upper rim of phosphonito-cavitand 1 and left a limited channel for small guest molecules or ions to enter the almost sealed cavity as illustrated in Figure 1.

5.2.2 Competitive Inclusion of Neutral Solvent Molecules

Calixresorcinarenes have been shown to be hosts for a variety of uncharged guest molecules, especially solvents. Since 2 has a cavity (~2Å radius) on the upper rim of the calixresorcinarene bowl as well as four flexible $PhCH_2CH_2$- groups which define a cavity at the bottom rim, the potential host properties of 2 for solvents have been investigated An unusual solvent inclusion phenomenon, including a competition between two solvent molecules for the cavity of the host 2, was observed by the ^1H NMR techniques. There are significant chemical shift differences in the ^1H NMR spectra of 2 in $(CD_3)_2CO$ and $CDCl_3$ as shown in Figure 2. When a small amount of $(CD_3)_2CO$ was added to a $CDCl_3$ solution of 2, the proton chemical shift, especially that H^4 (for the NMR labelling scheme, see structure 2 in Figure 2), shifted with increasing concentration of d_6-acetone (Table 1). It is obvious that there is a fast equilibrium between the host-guest pairs 2 $CDCl_3$ and 2.$(CD_3)_2CO$ such that an average chemical shift for the two complexes is observed. The large down field chemical shift changes of H^4 suggests that the included acetone is located at the lower rim, in the position shown in Figure 3.[1] The upper rim cavity is too small to accommodate an acetone molecule and if the acetone was included there, it probably would not affect the chemical shift of H^4 greatly

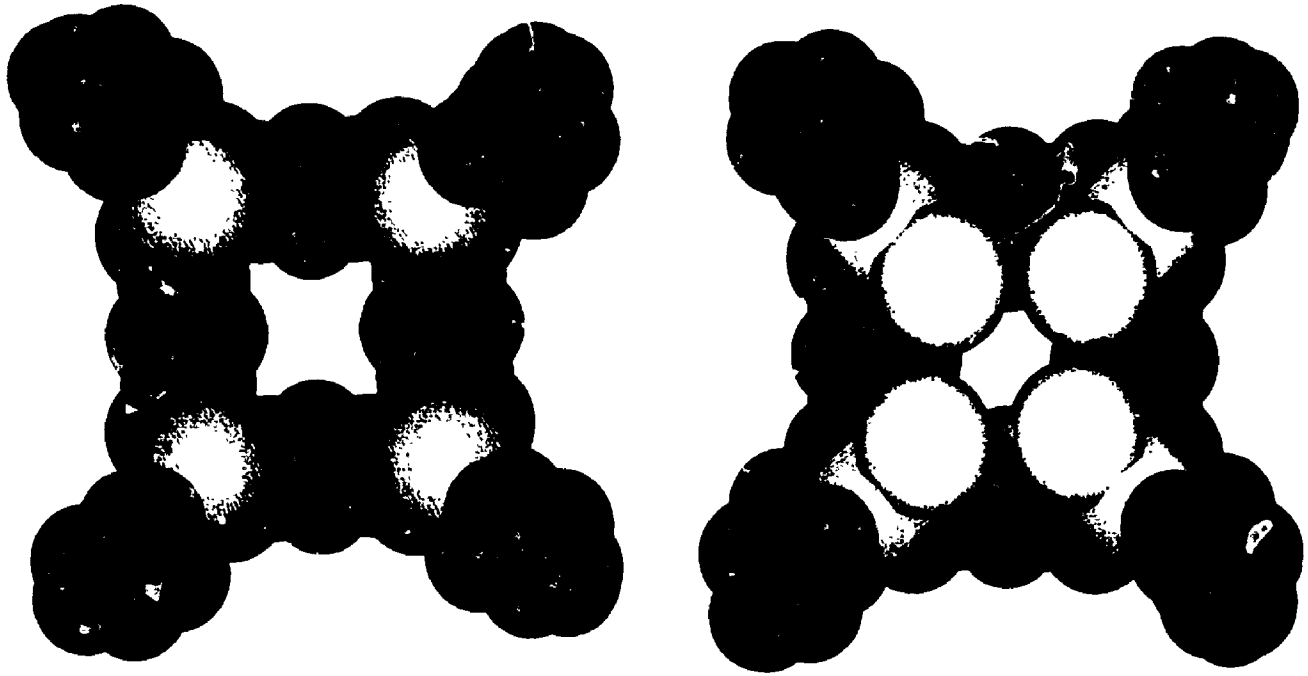


Figure 1. Space filling models of 1 and 2a showing the upper rim of the sealed bowl in 2a

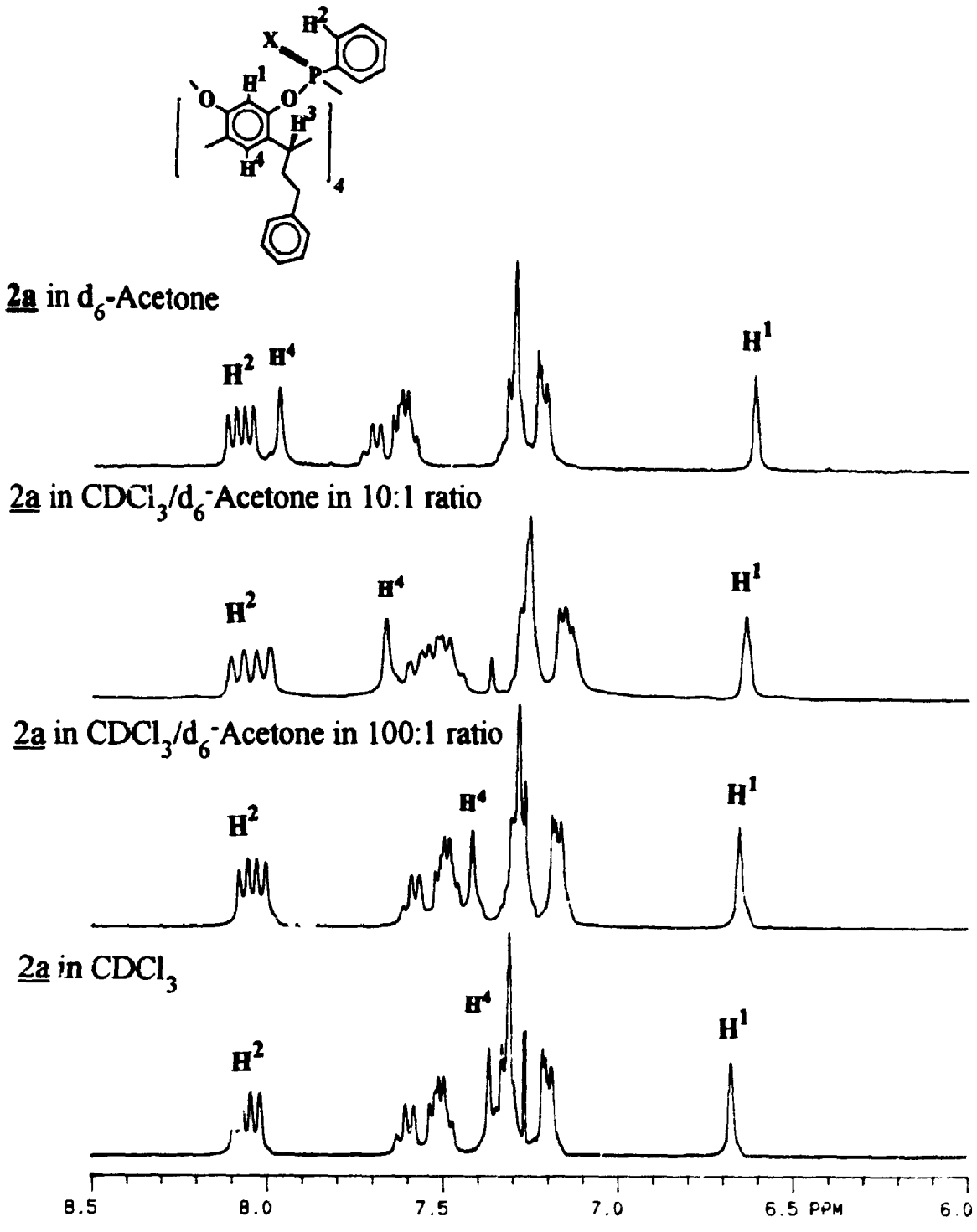


Figure 2. ^{1}H NMR spectra of **2a** in $CDCl_3$, d_6-Acetone and mixtures of $CDCl_3$ and d_6-Acetone

Table 1 Selected chemical shift differences [$300\times(\delta_{CDCl3\ or\ CD2Cl2} - \delta_{d6\text{-}Acetone})$] in $CDCl_3$ or CD_2Cl_2 and d_6-Acetone (for proton NMR labelling scheme, see Figure 2) for **2a** and **2b**

Host	Solvents	H^1	H^4	H^3	H^2
2a	$CDCl_3/d_6$-Acetone	+12Hz	-124Hz	-6Hz	-12Hz
2a	CD_2Cl_2/d_6-Acetone	+10Hz	-104Hz	+4Hz	-4Hz
2b	$CDCl_3/d_6$-Acetone	+10Hz	-126Hz	-10Hz	-10Hz
2b	CD_2Cl_2/d_6-Acetone	+8Hz	-106Hz	+2Hz	-2Hz

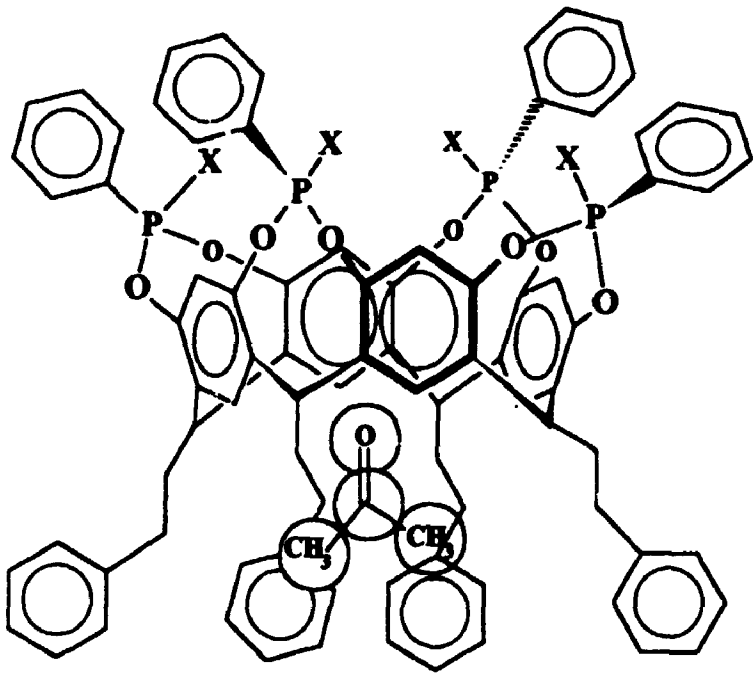


Figure 3. Proposed nature of solvent inclusions by **2a** and **2b** showing an acetone molecule inside the flexible $PhCH_2CH_2$- groups

5.2.3 Alkali Metal Ion Inclusion

The oxidation of **1** with sulphur or selenium not only resulted in a sealed bowl by bringing four X atoms (X = S and Se) to the upper rim of the calixresorcinarene bowl, but also introduced some 'soft' donor atoms (S, Se) for metal cation complexation and inclusion. The coordination chemistry of monophosphine sulphides and selenides has been extensively studied and multidentate phosphine sulphides and selenides have also attracted considerable interest recently.[2]

5.2.3.1 Alkali Metal Cation Liquid-liquid Extraction: The affinity of **2** towards metal cations has been investigated by using a liquid-liquid extraction test.[3] The results shown in Figure 4 indicate that **2** has a strong affinity for Cs^+. The selectivity of **2b** for Cs^+ is almost 4 times higher than for the other alkali cations. The highly selective cation inclusion of **2** may have applications in environmental pollution control and in radioactive cesium cation recovery from nuclear wastes.

5.2.3.2 Possible Structure of the Product of Alkali Cation Inclusion:

For understanding the possible structures of the cation inclusive complexes, **2a** was treated with a slurry of CsCl in acetone at room temperature. There are obvious differences between the ^1H NMR spectra of **2a** and **2a**.Cs^+ as shown in Figure 5. Cs^+ inclusion is very slow. 50% conversion from **2a** to **2a**.Cs^+ took about one week and it was difficult to reach 100% conversion. However, in the presence of a catalytic amount of KPF_6, Cs^+ inclusion could be completed. A pure Cs^+ inclusion product, **3** could be separated The

large down-field shift of the resonance of the ortho hydrogen (H^2) on the PPh group and down-field shift of the H^3 resonances suggested that the cesium cation formed an endo-calix complex as illustrated in Figure 6.[4] The arene rings at the edge of the calixresorcinarene bowl may also contribute to the binding of Cs^+. A strong parent ion peak (m/e = 1589, 100%; calc. 2aCs^+ = 1589) for 2aCs^+ in the FAB-MS spectrum of 3 supports the structure with endo-calix Cs^+ inclusion.

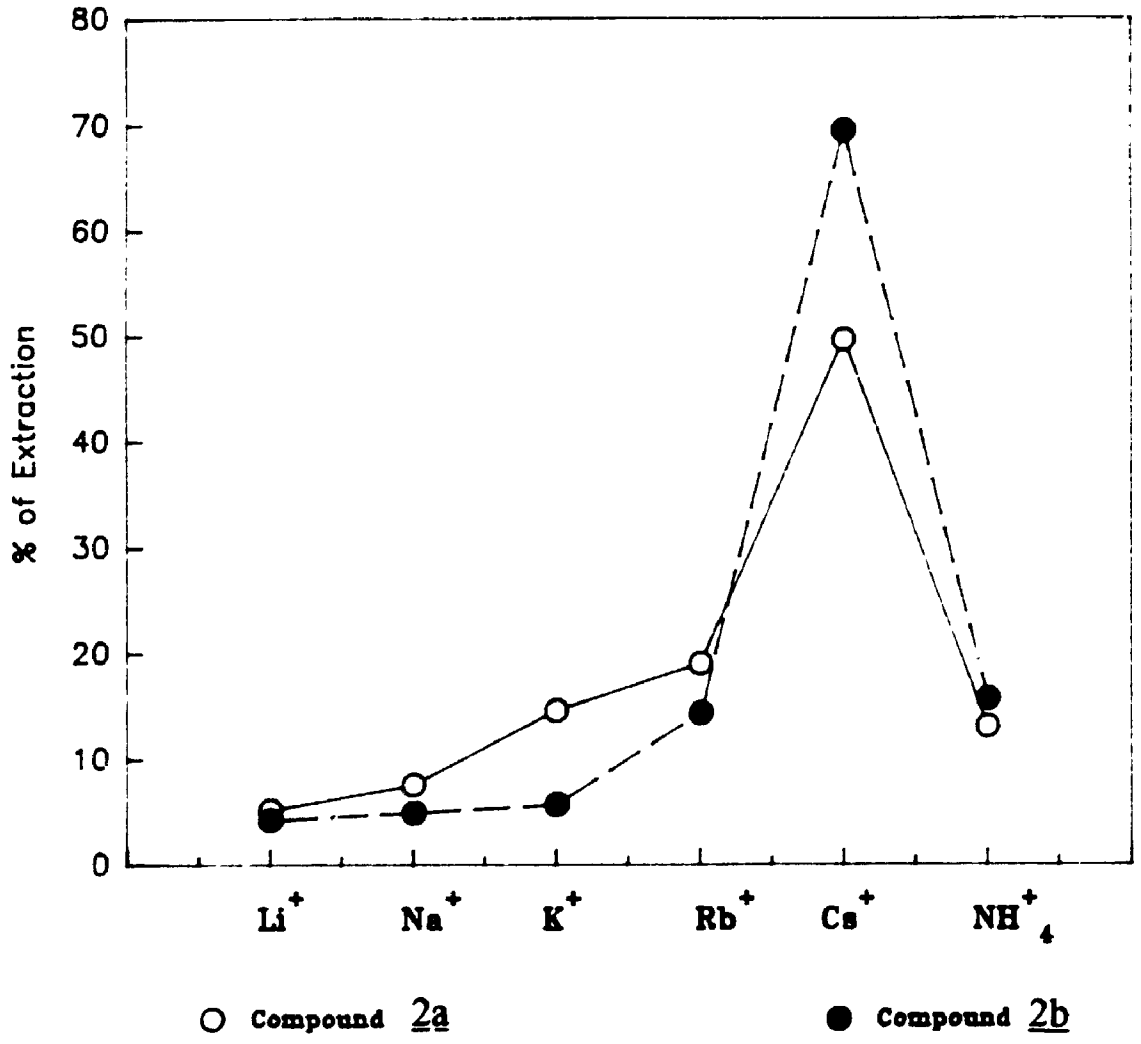


Figure 4. Extraction of alkali metal picrates in CH_2Cl_2 by calixresorcinarene derivatives 2a and 2b

Aqueous phase: [metal chloride] = 0.1M; [metal picrates] = 2.5×10^{-4}M.

Organic phase (CH_2Cl_2): [ligand] = 2.5×10^{-4}M.

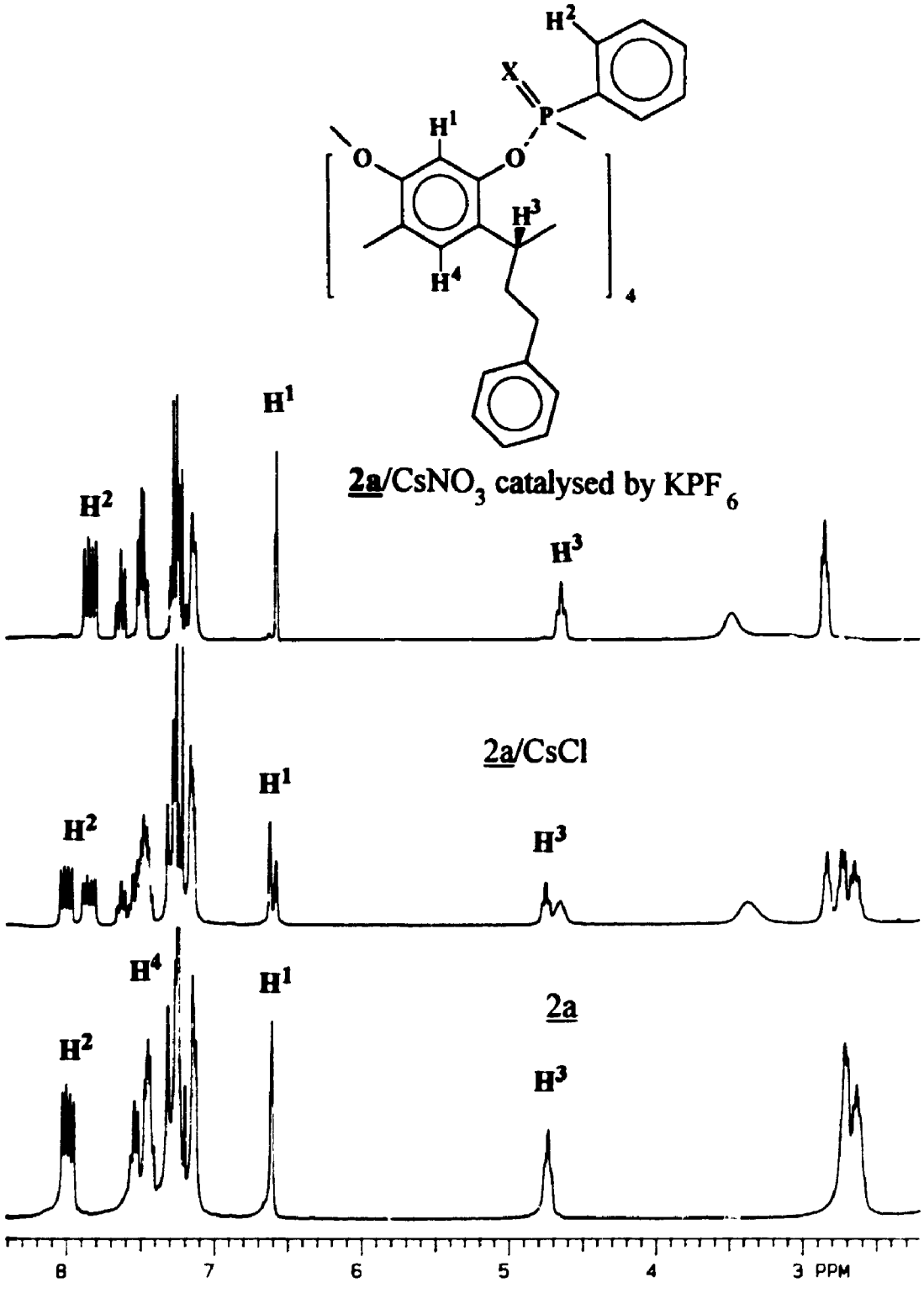


Figure 5. ^{1}H NMR spectra showing cesium cation inclusion by **2a**

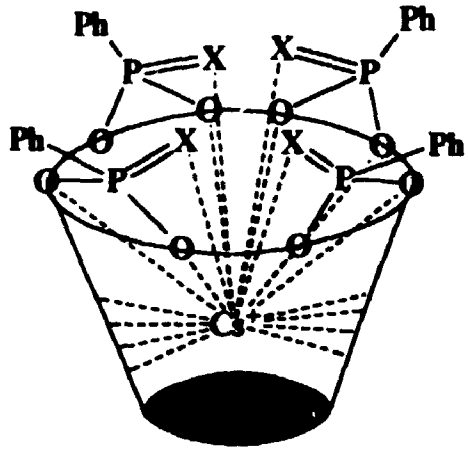


Figure 6. Proposed nature of endo-calix Cs^+ inclusion by 2

5.2.4 Other Metal Cation Inclusion by 2

In the presenc of macrocyclic ligands, the solubility of an inorganic salt in an organic phase will be increased owing to complexation and this could lead to numerous applications in both analytical chemistry and synthetic organic chemistry. Thus a study of complexation of other metal ions by 2 was made.

Treatment of 2 with AgO_2CCF_3 in a 1:4 stoichiometric ratio gave a crystalline product, 4. The complexation between 2 and Ag^+ was clearly indicated by dramatic chemical shift changes in the ^1H NMR spectra as illustrated in Figure 7. The ^{31}P NMR spectrum of 4 contained several signet. EDX and microanalysis results suggest that up to four Ag^+ ions could be involved in these compounds. If a different stoichiometric ratio of 2 and AgO_2CCF_3 was used, both the ^{31}P and the ^1H NMR spectra of the product also changed. Beautiful shiny crystals of 4 have been obtained from THF solution. However,

the crystals lost solvents extremely fast on removal from mother liquor and they did not diffract well. Without an X-ray structure, it is difficult to define the exact structure of 4. The complexation between 2 and AgO_2CCF_3 is reversible. For example, the AgO_2CCF_3 in 4 can be removed easily by washing with MeCN, indicating that the silver binding is weak and so that Ag^+ is not encapsulated inside the bowl

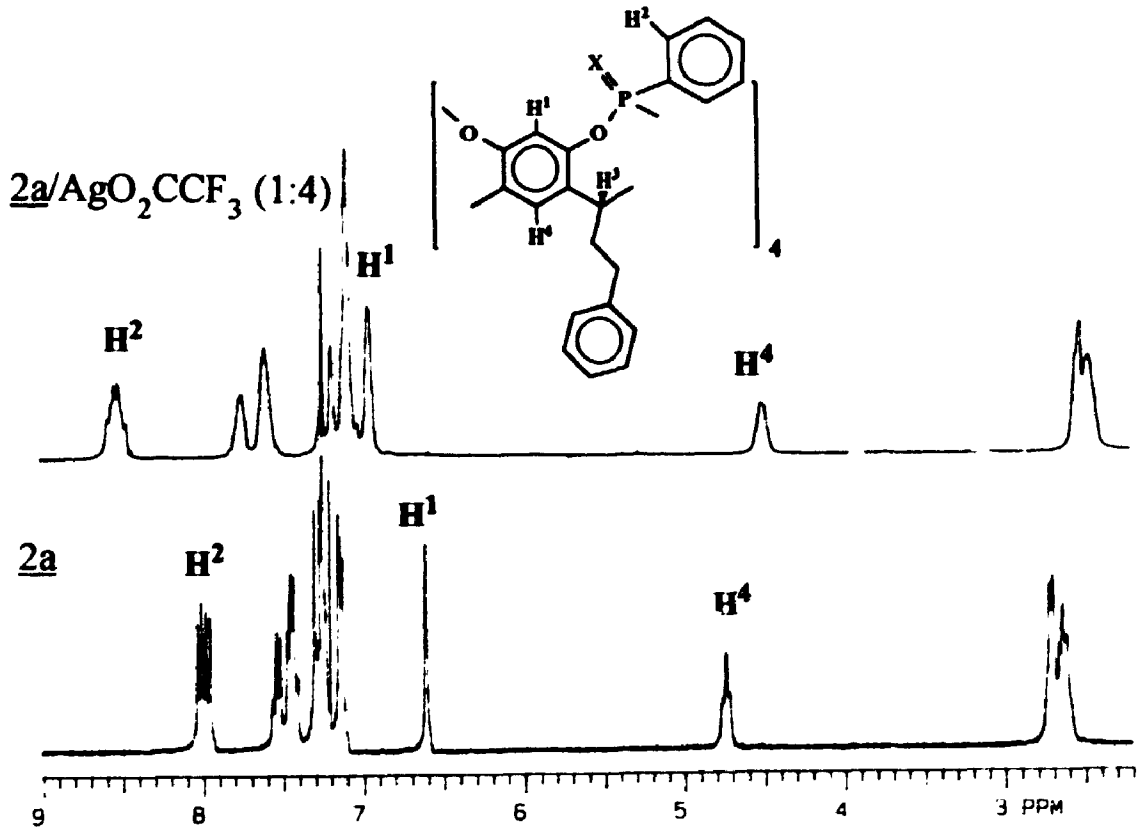


Figure 7. ^1H NMR spectra of 2a and 4 at room temperature in $CDCl_3$

Some other metal salts, such as $Cu(MeCN)_4PF_6$ and $Hg(O_2CCF_3)_2$ also react with **2** as indicated by spectroscopic studies. Thus, treatment of **2** with $Cu(MeCN)_4PF_6$ in 1:1 a stoichiometric ratio gave a product, **5a** which gave a singlet at $\delta = 85$ in the ^{31}P NMR spectrum whereas in 1:2 stoichiometric ratio it gave another product **5b** which showed a singlet at $\delta = 87$. Further increasing the concentration of $Cu(MeCN)_4PF_6$ did not lead to further changes to the ^{31}P NMR spectrum. The ^1H NMR spectrum of **5** indicated that all four MeCN ligands have been replaced, most likely by sulphide ligands in **2**. It is suggested that **2** can form 1:1 and 1:2 adducts with $Cu(MeCN)_4PF_6$ by replacement of MeCN ligands on the copper by the sulphide donors of **2**. Very similar phenomena were also observed on treatment of **2** with $Hg(O_2CCF_3)_2$ in 1:1 and 1:2 stoichiometric ratios. The exact structures of these complexes are still not clear at the present time.

5.3 EXPERIMENTAL SECTION

[Tetraphosphitocalixresorcinarene], **1**, was prepared as described in Chapter 2. All the experiments were carried out under the conditions described in Chapter 2 All the spectroscopic data were recorded by using the same instruments listed in Chapter 2.

5.3.1 Cation Extraction

Two phase cation extraction was carried out between water solution (5mL) containing [alkali metal picrate] = 2.5×10^{-4}M and [MCl] = 0.1M and a solution of **2** (2.5×10^{-4}M) in

$CHCl_3$. The two-phase mixture was shaken for 5min at 23°C. The extractability was determined spectrophotometrically at 357nm from the decrease in the absorbance of the picrate ion in the aqueous phase. No picrate extraction was observed in the absence of receptor.

5.3.2 [Calixresorcinarene.P_4S_4], 2a

A mixture of [Calixresorcinarene.P_4], 1, (0.5g, 0.38mmol) and elemental sulphur (0.12g, 3.8mmol) in $CHCl_3$ (20mL) was stirred at room temperature for 48h. The $CHCl_3$ was then removed completely under vacuum. The residue was redissolved in CH_2Cl_2 (5mL) and unreacted sulphur was removed by filtration. The product was precipitated by adding MeCN (20mL). The white precipitate was filtered, washed with CCl_4 (5mL×2) to remove traces of excess sulphur and dried under vacuum. Small amounts of pure sample can be obtained by column chromatography on silica gel with hexane then Et_2O/hexane (1:1) as eluent. A white solid was obtained. Yield: 0.42g, 76%. Anal. Calc. for 2a $C_{84}H_{68}O_8P_4S_4$: C, 69.2; H, 4.7; Found: C, 68.9; H, 4.6%. NMR in $CDCl_3$: $\delta(^{31}P\{^1H\})$ = 81.2 [s]; $\delta(^1H)$ = 2.65-2.75 [m, 8H, $CH_2C\underline{H}_2Ph$], 2.75-2.85 [m, 8H, $C\underline{H}_2CH_2Ph$], 4.80 [br, 4H, $C\underline{H}(CH_2)_2Ph$], 6.67 [t, $^4J_{PH}$ = 2.2 Hz, 4H, Ar$\underline{H}$, ortho to O], 7.15-7.20 [m, 8H, $C_6\underline{H}_5$], 7.27-7.33 [m, 12H, $C_6\underline{H}_5$], 7.36 [s, 4H, Ar$\underline{H}$, meta to O], 7.43-7.60 [m, 12H, $PC_6\underline{H}_5$, para and meta to P], 7.99-8.10 [m, 8H, $PC_6\underline{H}_5$, ortho to P]. FAB-MS: m/e = 1458 [MH_2^+, 100%].

$\delta(^1H)$ in d_6-acetone: 2.81 [br, 16H, $C\underline{H}_2C\underline{H}_2Ph$], 4.83 [br, 4H, $C\underline{H}(CH_2)_2Ph$], 6.61 [t, $^4J_{PH}$

= 2.2Hz, 4H, Ar<u>H</u>, ortho to O], 7.30 [m, br, 20H, $C_6\underline{H}_5$], 7.98 [s, 4H, Ar<u>H</u>, meta to O], 7.61-7.71[m, 12H, $PC_6\underline{H}_5$, para and meta to P], 8.05-8.12 [m, 8H, $PC_6\underline{H}_5$, ortho to P].

5.3.3 [Calixresorcinarene.P_4Se_4], <u>2b</u>

A mixture of [Calixresorcinarene.P_4], <u>1</u> (0.5g, 0.38mmol) and elemental selenium (powder) (0.3g, 3.8mmol) in $CHCl_3$ (20mL) was stirred at room temperature for 48h. By using the same procedure as above, a white solid was obtained. Yield: 0.43g, 68.7%. Anal. Calc for <u>2b</u> $C_{84}H_{68}O_8P_4Se_4$: C, 61.2; H, 4.2; Found: C, 61.0; H, 4.2%. NMR in $CDCl_3$: $\delta(^{31}P)$ = 86.6 [s, $^1J(^{31}P\text{-}^{77}Se)$ = 473Hz); $\delta(^1H)$ = 2.63-2.75 [m, 16H, $C\underline{H}_2C\underline{H}_2Ph$], 4.76 [br, 4H, $C\underline{H}(CH_2)_2Ph$], 6.65 [t, $^4J_{PH}$ = 2.1Hz, 4H, Ar<u>H</u>, ortho to O], 7.15-7.22 [m, 8H, $C_6\underline{H}_5$], 7.27-7.31 [m, 12H, $C_6\underline{H}_5$], 7.35 [s, 4H, Ar<u>H</u>, meta to O], 7.43-7.59 [m, 12H, $PC_6\underline{H}_5$, para and meta to P], 7.98-8.10 [m, 8H, $PC_6\underline{H}_5$, ortho to P]. FAB-MS: m/e = 1645 [MH^+, 100%].

$\delta(^1H)$ in d_6-acetone: 2.73-2.95 [br, 16H, $C\underline{H}_2C\underline{H}_2Ph$], 4.81 [br, 4H, $C\underline{H}(CH_2)_2Ph$], 6.60 [t, $^4J_{PH}$ = 2.2Hz, 4H, Ar<u>H</u>, ortho to O], 7.20-7.22 [m, 8H, $C_6\underline{H}_5$], 7.25-7.33 [m, 12H, $C_6\underline{H}_5$], 7.98 [s, 4H, Ar<u>H</u>, meta to O], 7.50-7.73 [m, 12H, $PC_6\underline{H}_5$, para and meta to P], 8.06-8.13 [m, 8H, $PC_6\underline{H}_5$, ortho to P].

5.3.4 [CalixresorcinareneP_4S_4Cs]NO_3, <u>3</u>

A suspension of $CsNO_3$ (0.4g, 2mmol), KPF_6 (0.005g, 0.027mmol) and

[CalixresorcinareneP$_4$S$_4$], **2a** (0.2g, 0.14 mmol) in acetone (20mL) was stirred at room temperature for 48h. The suspension was filtered. The solid was washed with acetone twice (5mL×2) and dried under vacuum. Then the solid was redissolved in CH_2Cl_2 (5mL) and the solution was filtered again to remove excess metal salts. MeCN was diffused into the filtrate, giving a white solid precipitate, which was washed with MeCN and dried under vacuum. Yield: 0.20g, 87%. Anal. Calc for **3** $C_{84}H_{68}Cs_1N_1O_{11}P_4S_4$: C, 61.1; H, 4.1; Found: C, 60.8; H, 3.9%. NMR in $CDCl_3$: $\delta(^{31}P)$ = 83.4 (s); $\delta(^1H)$ = 2.86 [s, br, 8H, CH_2CH_2Ph], 3.50 [br, 8H, CH_2CH_2Ph], 4.66 [t, 4H, $CH(CH_2)_2Ph$], 6.60 [s, 4H, ArH, ortho to O], 7.17-7.32, 7.47-7.54, 7.63-7.68, 7.82-7.86 [m, 40H, C_6H_5 and 4H, ArH, meta to O]. FAB-MS:m/e 1589 [**2a**.Cs$^+$, 100%].

5.3.5 [CalixresorcinareneP$_4$S$_4$(AgO$_2$CCF$_3$)$_4$], 4a

A mixture of AgO_2CCF_3 (0.13g, 0.59mmol) in MeCN (5mL) and [CalixresorcinareneP$_4$S$_4$], **2a** (0.2g, 0.14mmol) in THF (20mL) was stirred at room temperature for 2h. All the solvent was removed under vacuum. The solid was redissolved in THF (10mL). A MeCN solution containing AgO_2CCF_3 (0.01g/10mL) was slowly diffused into the THF solution of the residue. Well-shaped shining crystals were obtained. The crystals were isolated, washed with a small portion of MeCN (containing AgO_2CCF_3, 0.01g/5mL) and hexane and then dried under vacuum. A white powder was obtained. Yield: 0.25g, 80.9%. Anal. Calc for **4a** $C_{92}H_{68}Ag_4F_{12}O_{16}P_4S_4$: C, 47.3; H, 2.9; Found: C, 46.9; H, 3.1%. NMR in $CDCl_3$: $\delta(^{31}P)$ at room temperature, 80.4 [s], 81.0 [s], 81.7 [s]; $\delta(^{31}P\{^1H\})$ at -60°C, 80.9 [s]; $\delta(^1H)$ = 2.54 [br, 16H, CH_2CH_2Ph], 4.49 [t, 4H,

C<u>H</u>$(CH_2)_2$Ph], 6.95-7.78 [m, 32H, $C_6\underline{H}_5$ and 8H, Ar<u>H</u>], 8.50-8.60 [m, 8H, $PC_6\underline{H}_5$, ortho to P]. FAB-MS:m/e 1565 [MAg^+, 100%], 1674 [MAg_2^+, 10%]. ν_{C-O}= 1658cm^{-1}.

5.3.6 [CalixresorcinareneP$_4$Se$_4$(AgO_2CCF_3)$_4$], <u>4b</u>

A mixture of AgO_2CCF_3 (0.110g, 0.5mmol) in MeCN (5mL) and [CalixresorcinareneP$_4$Se$_4$], <u>2b</u> (0.2g, 0.12mmol) in THF (20mL) was stirred at room temperature for 2h. By using the same procedure as mentioned above, a white powder was obtained. Yield: 0.23g, 75%. Anal. Calc for <u>4b</u> $C_{92}H_{68}Ag_4F_{12}O_{16}P_4Se_4$: C, 43.7; H, 2.7; Found: C, 43.5; H, 2.4%. NMR in $CDCl_3$: $\delta(^{31}P)$ = 88 [m]; $\delta(^1H)$ = 2.54 [br, 16H, C<u>H</u>$_2$C<u>H</u>$_2$Ph], 4.54 [t, 4H, C<u>H</u>$(CH_2)_2$Ph], 6.94-7.80 [m, 32H, $C_6\underline{H}_5$ and 8H, Ar<u>H</u>], 8.50-8.57 [m, 8H, $PC_6\underline{H}_5$, ortho to P]. FAB-MS:m/e 1754 [MAg^+, 100%]. ν_{C-O}=1658 cm^{-1}.

5.3.7 [CalixresorcinareneP$_4$S$_4$($AgPF_6$)], <u>4c</u>

A mixture of $AgPF_6$ (0.0347g, 0.14mmol) in MeCN (5mL) and [CalixresorcinareneP$_4$S$_4$], <u>2a</u> (0.200g, 0.14mmol) in THF (20mL) was stirred at room temperature for 2h. All the solvent was removed under vacuum. The solid residue was then washed with a small portion of MeCN (containing $AgPF_6$, 0.01g/5mL) and dried under vacuum. A white powder was obtained. Yield: 0.23g, 96%. Anal. Calc. for <u>4c</u> $C_{84}H_{68}Ag_1F_6O_8P_5S_4$: C, 59.0; H, 4.0; Found: C, 58.7; H, 3.6%. NMR in $CDCl_3$: $\delta(^{31}P\{^1H\})$ at room temperature, 84.2 [s]; $\delta(^1H)$ = 2.88 [br, 8H, $CH_2C\underline{H}_2$Ph], 3.09 [br, 8H, $C\underline{H}_2CH_2$Ph], 4.56 [t, 4H, C<u>H</u>$(CH_2)_2$Ph], 6.53 [s, 4H, Ar<u>H</u>, ortho to O], 7.11-7.73 [m, 40H, $C_6\underline{H}_5$], 7.84-7.92 [m,

8H, $PC_6\underline{H}_5$, ortho to P], 8.23 [s, 4H, Ar$\underline{H}$, meta to O]. FAB-MS m/e 1565 [MAg$^+$, 100%]

5.3.8 [CalixresorcinareneP$_4$S$_4$(CuPF$_6$)$_n$], **5a** (n =1) and **5b** (n=2)

A mixture of $Cu(MeCN)_4PF_6$ (0.052g, 0.14mmol) and [CalixresorcinareneP$_4$S$_4$], **2a** (0.2g, 0.14mmol) in CH_2Cl_2 (20mL) was stirred at room temperature for 2h. All the solvent was removed under vacuum. The solid residue was washed with hexane. A white solid was obtained. Yield: 0.22g, 94%. Anal. Calc for **5a** $C_{84}H_{68}Cu_1F_6O_8P_4S_4$: C, 60.6; H, 4.1; Found: C, 60.3; H, 3.9%. NMR in $CDCl_3$: $\delta(^{31}P)$ = 85.3[s]; $\delta(^1H)$ = 2.9 [br, 8H, $CH_2C\underline{H}_2Ph$], 3.1 [br, 8H, $C\underline{H}_2CH_2Ph$], 4.55 [br, 4H, $C\underline{H}(CH_2)_2Ph$], 6.55 [br, 4H, Ar$\underline{H}$, ortho to O], 7.18-8.40 [m, 48H, $C_6\underline{H}_5$, Ar$\underline{H}$, meta to O]. If $Cu(MeCN)_4PF_6$ (0.105g, 0.28mmol) was used, **5b** was obtained in the same manner. Yield: 0.25g, 95%. Anal. Calc for **5b** $C_{84}H_{68}Cu_2F_{12}O_8P_6S_4$: C, 53.8; H, 3.7; Found: C, 53.5; H, 3.3%. NMR in $CDCl_3$: $\delta(^{31}P)$ = 88.4 [s]; $\delta(^1H)$ = 2.07 [s, 6H, $C\underline{H}_3CN$], 2.88 [br, 8H, $CH_2C\underline{H}_2Ph$], 3.12 [br, 8H, $C\underline{H}_2CH_2Ph$], 4.52 [br, 4H, $C\underline{H}(CH_2)_2Ph$], 6.58 [br, 4H, Ar$\underline{H}$, ortho to O], 7.10-8.37 [m, 48H, $C_6\underline{H}_5$, Ar$\underline{H}$,].

5.4 REFERENCES

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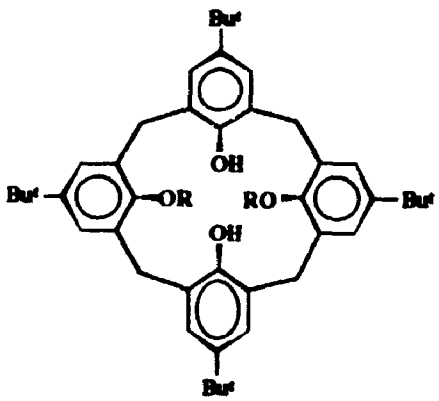
Chapter Six

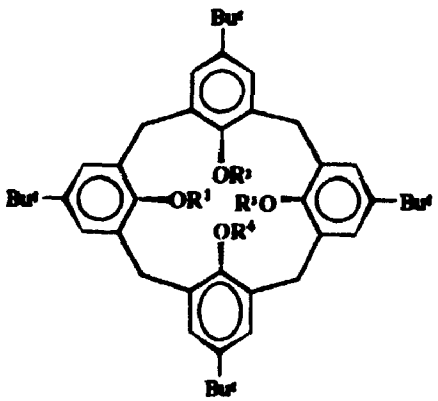
CALIXARENES: AN INCLUSION COMPOUND AND SOME TRANSITION METAL RIMMED DERIVATIVES

6.1 INTRODUCTION

In previous chapters, some calixresorcinarene derivatives with transition metals on the upper rim which showed unique anion recognition properties have been discussed. In the calixarene family, there is another important member, *p-tert*-butylcalix[4]arene 1. In contrast to calix[4]resorcinarene, calixarene 1 carries four hydroxyl groups at its bottom rim and these provide suitable functional groups to enable the introduction of a transition metal rim at its bottom. In this chapter, the synthesis of the tridentate phosphinito-calix[4]arene derivative 2c and some *p-tert*-butylcalix[4]arenes with transition metals on the lower rim, 3, will be reported. The conformations of the calixarenes with transition metal substituents on the lower rim and their host-guest properties will be discussed and compared with a complex of 1a with acetonitrile.



1 (1a: R=H; 1b: R=Me)



2a: $R^1=R^2=R^3=R^4=PPh_2$;
2b: $R^1=R^2=Me$; $R^3=R^4=PPh_2$
2c: $R^1=R^2=R^3=PPh_2$; $R^4=H$

6.2 RESULTS AND DISCUSSION

6.2.1 Endo-calix Acetonitrile Complex of *p-tert*-Butylcalix[4]arene

The calixarene system is known to be a clathrating agent for organic molecules.[1-3] The determination of the crystal structure of **1a**.MeCN affords yet another illustration of this property. The crystal structure of **1a**.MeCN is shown in Figure 1 and selected bond distances and angles are listed in Table 1. The calixarene host is centred around a crystallographic C_4 axis in the expected symmetrical cone conformation. The linear guest molecule occupies the resulting bowl-shaped cavity; its C and N atoms lie on the central C_4 axis of the calix with the methyl group directed towards the lower rim formed by the four hydroxyl groups as illustrated in Figure 1. The acetonitrile C-C and C-N bond lengths [1.53(1) and 1.26(1) Å] which are sufficiently different from accepted values [1.47 and 1.14 Å],[4] suggest that the positions of the atoms C(29), C(28) and N(27) are subject to systematic error which may arise from the complications caused by twinning. Some caution is therefore necessary in the interpretation of the shortest contacts between the host and the guest atoms C(29), C(28) and N(27), namely C(29)...C(2) 3.776(4) and C(28)...C(16) 4.449(3) Å; N(27) is more than 5.0 Å from any C or O atom of its host calixarene. These distances suggest that the acetonitrile methyl group is wedged into the bowl of **1a**, whereas the environments of C(28) and N(27) are more open.

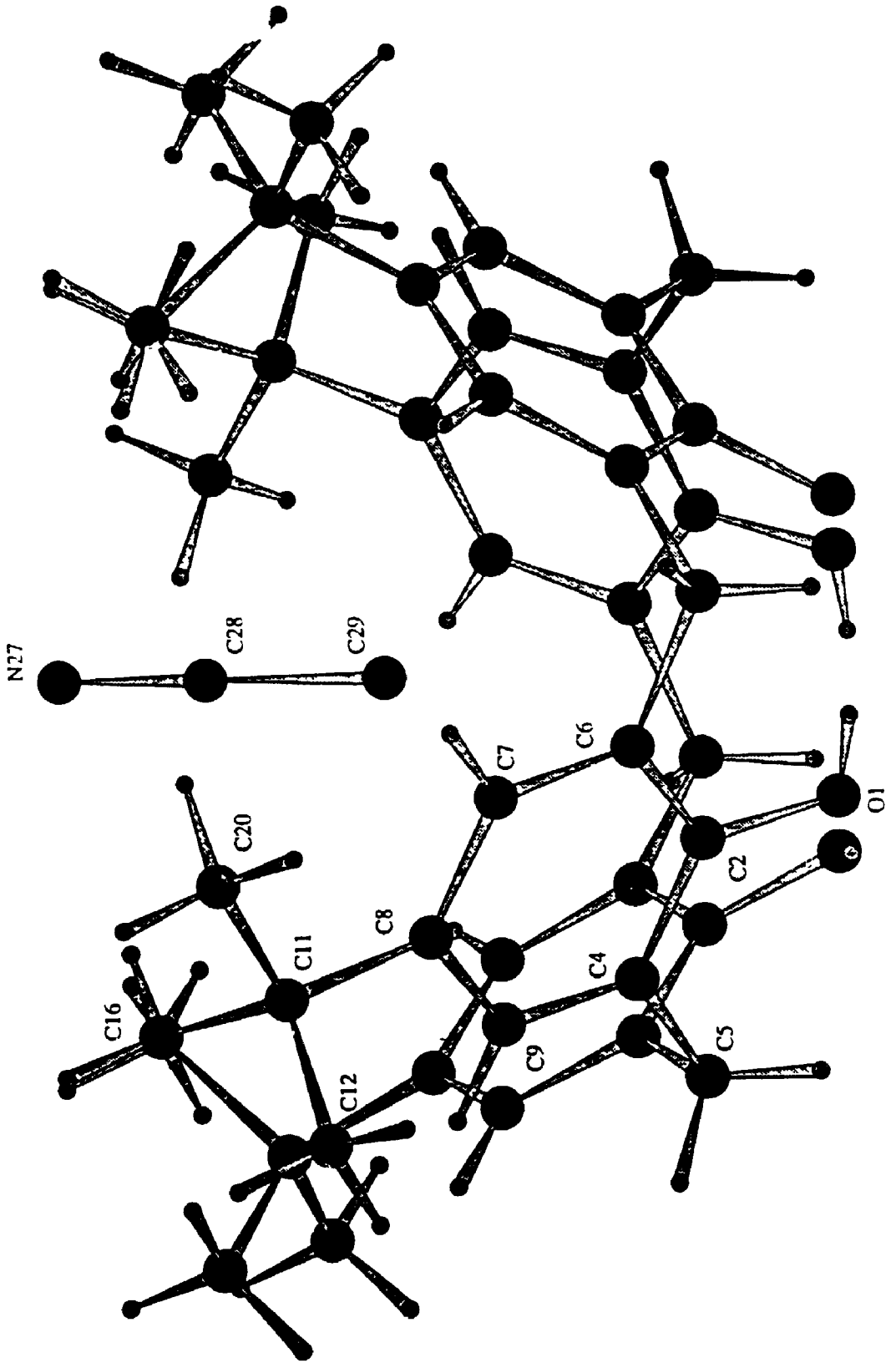


Figure 1. A view of the t-butylcalix[4]arene host and its acetonitrile guest

Table 1. Selected interatomic distances (Å) and angles (°)

(a) Bond lengths:

C(2)-C(4)	1.400(2)	C(2)-C(6)	1.393(2)	C(4)-C(5')	1.520(2)
C(4)-C(9)	1.391(2)	C(5)-C(6)	1.521(2)	C(6) - C(7)	1.402(2)
C(7)-C(8)	1.389(2)	C(8) - C(9)	1.398(2)	C(8)-C(11)	1.533(3)
C(11) - C(12)	1.535(4)	C(11)-C(16)	1.540(4)	C(11) - C(20)	1.527(4)
C(28)-C(29)	1.532(11)	O(1) - C(2)	1.385(2)	C(28)-N(27)	1.263(13)

(b) Bond angles:

C(29) - C(28) - N(27)	180.0(2)	O(1) - C(2) - C(4)	117.4(2)
O(1) - C(2) - C(6)	121.4(2)	C(4) - C(2) - C(6)	121.1(2)
C(2) - C(4) - C(5')	121.8(2)	C(2) - C(4) - C(9)	118.3(2)
C(5')- C(4) - C(9)	119.8(2)	C(4")- C(5) - C(6)	111.6(2)
C(2) - C(6) - C(5)	121.9(2)	C(2) - C(6) - C(7)	118.3(2)
C(5) - C(6) - C(7)	119.8(2)	C(6) - C(7) - C(8)	122.4(2)
C(7) - C(8) - C(9)	117.2(2)	C(7) - C(8) - C(11)	123.3(2)
C(9) - C(8) - C(11)	119.5(2)	C(4) - C(9) - C(8)	122.6(2)
C(8) - C(11) - C(12)	109.0(2)	C(8) - C(11) - C(16)	109.5(2)
C(8) - C(11) - C(20)	112.4(2)	C(12) - C(11) - C(16)	109.0(2)
C(12) - C(11) - C(20)	108.3(3)	C(16) - C(11) - C(20)	108.7(2)

The symmetrical cone conformation of **1a** found here may be characterised by the dihedral angle of 123.1° between the phenyl ring plane and that of the four hydroxyl oxygen atoms; similar values of 122.6° - 125.8° have been found for the corresponding angles in **1a**.toluene[5], **1a**.dimethyl sulphoxide[6], (**1a**)$_2$.anisole[7] and (**1a**-H).Cs(MeCN)[8]. In all of these complexes the **1a** host has exact C_4 symmetry and the disordered guest straddles the central C_4 symmetry axis of the calix cavity. As has been found in the structures of other calixarene complexes the hydroxyl rim of the calix cavity in **1a**.MeCN is supported by O-H...O hydrogen bonds, although the O(1)...O(1) separation of 2.692(2) Å is slightly greater than corresponding values in related complexes [e.g. 2.670(9) Å in **1a**.toluene and 2.652(4) and 2.654(5) Å in (**1a**)$_2$.anisole].

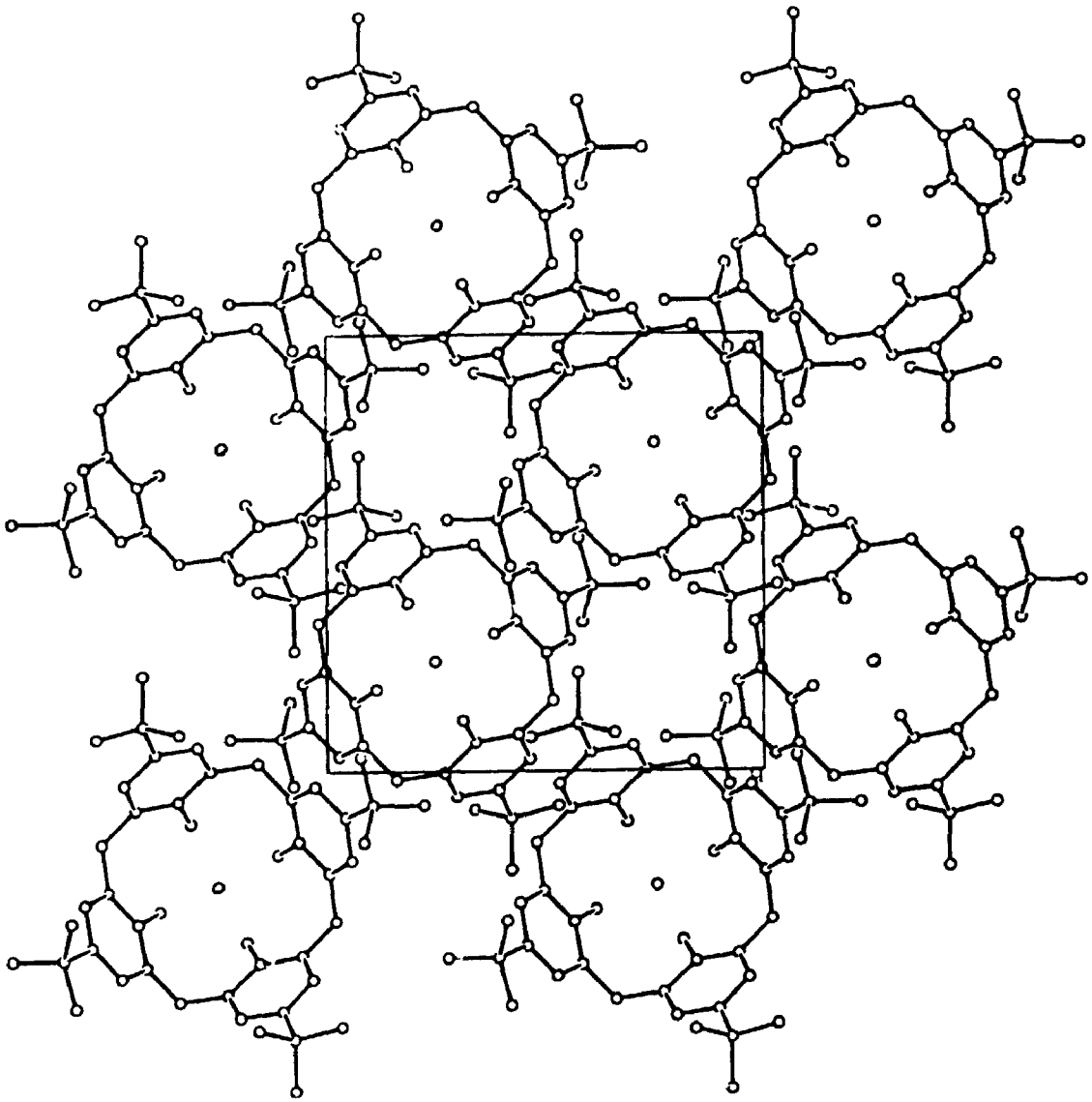


Figure 2 The unit cell contents of **1a**·MeCN crystals viewed in projection down c The cell origin is at the lower left corner, a is horizontal and b is vertical.

Bond lengths and angles within **1a** (Table 2) are unexceptional. The phenyl carbon atoms are coplanar to within 0.005(2) Å and the internal ring angles at C-substituted C(4), C(6) and C(8) are all ca. 2° less than 120° O(1) and C(11) are displaced by 0.04 - 0.06 Å from the phenyl ring away from the C_4 axis and C(5) is displaced towards the axis by 0.04 Å. The t-butyl group has staggered conformations across its C-CH_3 bonds and its orientation brings C(20) close to the plane of the phenyl ring.

The crystal packing in **1a**.MeCN (Figure 2) contains two types of channel running parallel to the c-axis: the wider channels are centred on the four-fold symmetry axes and contain the guest MeCN molecules; in addition, there are channels centred on the bar-4 axes at (3/4, 1/4, z) and (1/4, 3/4, z) which are evidently too narrow to accommodate even small guest molecules. There are only three **1a**..**1a** contacts involving non-hydrogen atoms which are 0.1 Å less that the sum of the appropriate van der Waals radii: C(2)...C(5i) 3.497(2), C(5)...C(6i) 3.483(2) and C(12)...C(20ii) 3.789(4) Å (i: -x, -y, -z, ii: -1/2-y, x, z).

The structure is important as a model for the calixarene part of the more complex molecules described below which, though they were often obtained in crystalline form, always failed to diffract sufficiently to allow X-ray structure determination. Instead it is necessary to rely on spectroscopic techniques, comparing the NMR spectra with that of the parent calixarene whose structure is known (Figure 1).

6.2.2 Synthesis and Structure of the Tridentate Phosphinito Calix[4]arene Derivative, 2c

Since polydentate ligands play an important role in coordination chemistry, the preparation of new polydentate ligands with unusual geometry, which may then coordinate to transition metals in unusual ways, is highly desirable. Both fully hydroxylated **1a** and partially hydroxylated *tert*-butylcalixarene **1b** have been reacted with chlorodiphenylphosphine to give the fully substituted[9] and partially substituted[10] diphenylphosphinitocalix[4]arenes, **2a** and **2b**. The compound **2a** was used as a phosphorus donor ligand in forming copper(I)[9] and iron(0) carbonyl[11] complexes. However, this ligand **2a** is unstable towards hydrolysis by traces of water. It also decomposes quickly when dissolved in the NMR solvent $CDCl_3$. By changing reaction conditions, the ligand **2c** with three PPh_2 donors at the bottom rim of the calixarene can be obtained in high yield. Its ^1H NMR spectrum shows three Bu^t groups at δ 1.2, 1.1 and 1.15 in 1:1:2 ratio, corresponding to three different Bu^t environments. The methylene groups also show four sets of doublet resonances.[1] The $^{31}P\{^1H\}$ NMR spectrum contained only two singlet resonances in a 2:1 ratio, as expected for **2c** in the cone conformation. Less symmetrical conformations can be discounted on this basis. The presence of the hydroxy group also was confirmed by the IR spectrum, which gives ν(OH) at 3351cm^{-1}. The higher stability of **2c** than **2a** is attributed to steric relief when there is one less bulky PPh_2 group present.

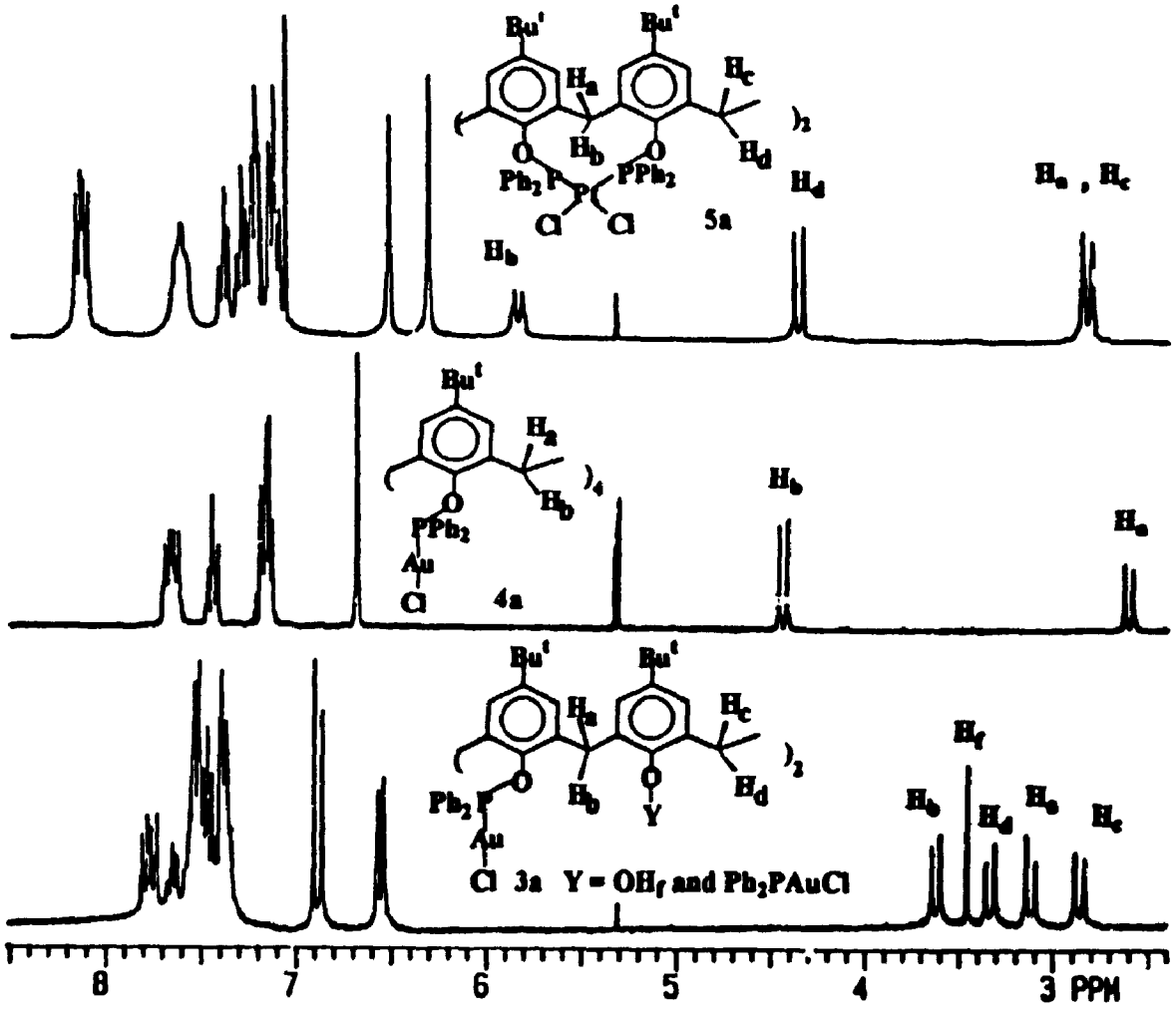


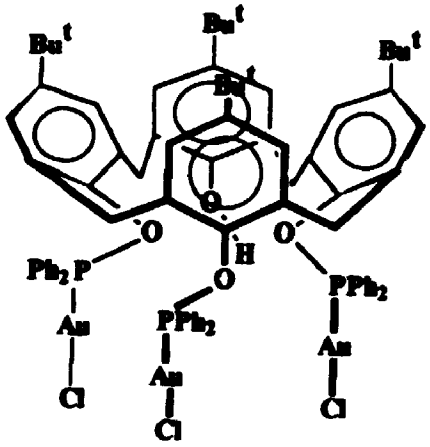
Figure 3. The ^{1}H NMR spectra of 3, 4a and 5a
(resonances due to the t-butyl groups are omitted for clarity).

6.2.3 Coordination Chemistry of 2c and 2a

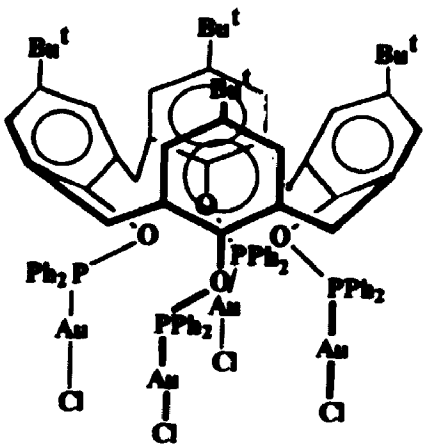
It is expected that 2c and 2a will show different coordination to transition metals. Thus, treatment of 2c with [AuCl(SMe$_2$)] gave a conformer of 3. The three PAuX units are not identical. The $^{31}P\{^1H\}$ NMR spectrum shows two singlets at δ = 114.8 (s) and δ = 117.8 (s). The observation of four pairs of methylene resonances and three singlet Bu^t resonances clearly supports the proposed structure with three PPh$_2$ substituents (see Figure 3a). The FTIR spectrum also confirmed that the ArOH group was still present from the absorption band at ν(OH) = 3366 cm^{-1}. Although a fresh crystal of 3 dried in current of N_2, contains MeCN molecules in 1:1 ratio as indicated by the ^1H NMR spectrum, the MeCN can be removed within 48h by placing crystalline 3 under vacuum (0.01mm-Hg). The MeCN can be either held loosely in the cavity of the calixarene or simply located in the crystalline lattice. Hence the question of the ability of the complexes to act as hosts for small molecules such as MeCN could not be answered with certainty.

In order to compare the behavioral difference between the tridentate phosphinito-calix[4]arene 2c and the tetradentate 2a, compound 2a has also been coordinated with some later transition metals. Thus, treatment of 2a with [AuCl(SMe$_2$)] or [(AuCCPh)$_n$] gave the air and moisture stable tetrametal complexes, 4 (4a, X = Cl, 4b, X = CCPh), containing one gold(I) per phosphorus atom. The four PAuX units are now identical as shown by the ^{31}P NMR spectra [δ = 105 (s), X = Cl; δ = 135 (s), X = CCPh]. The complexes are highly symmetric and contain a golden rim at the bottom of the calix[4]arene. Since the bridging CH$_2$ groups may serve as spectroscopic probes,[1] the

structures and conformations of **4** are clearly indicated by their ^{1}H NMR spectra (see Figure 3b). There is only one pair of methylene signals, indicating that the calixarene bowls are still in the cone conformation. The inclusion behaviour of **4** is not as obvious as with other calixarenes.[1] Based upon a molecular mechanics calculation,[12] the bulky PPh_2AuCl substituents should cause the aryl rings of the calixarene bowl to be closer to vertical than in **1**, and therefore the four tert-butyl groups should be forced together such that the entrance of the bowl will be restricted, thus only allowing the entry of small guest molecules (see Figure 4). Nevertheless, the complexes **4** crystallize with MeCN, which may be present inside the bowl, as in the precursor **1** (Figure 1).



Structure of **3**



Structure of **4a**

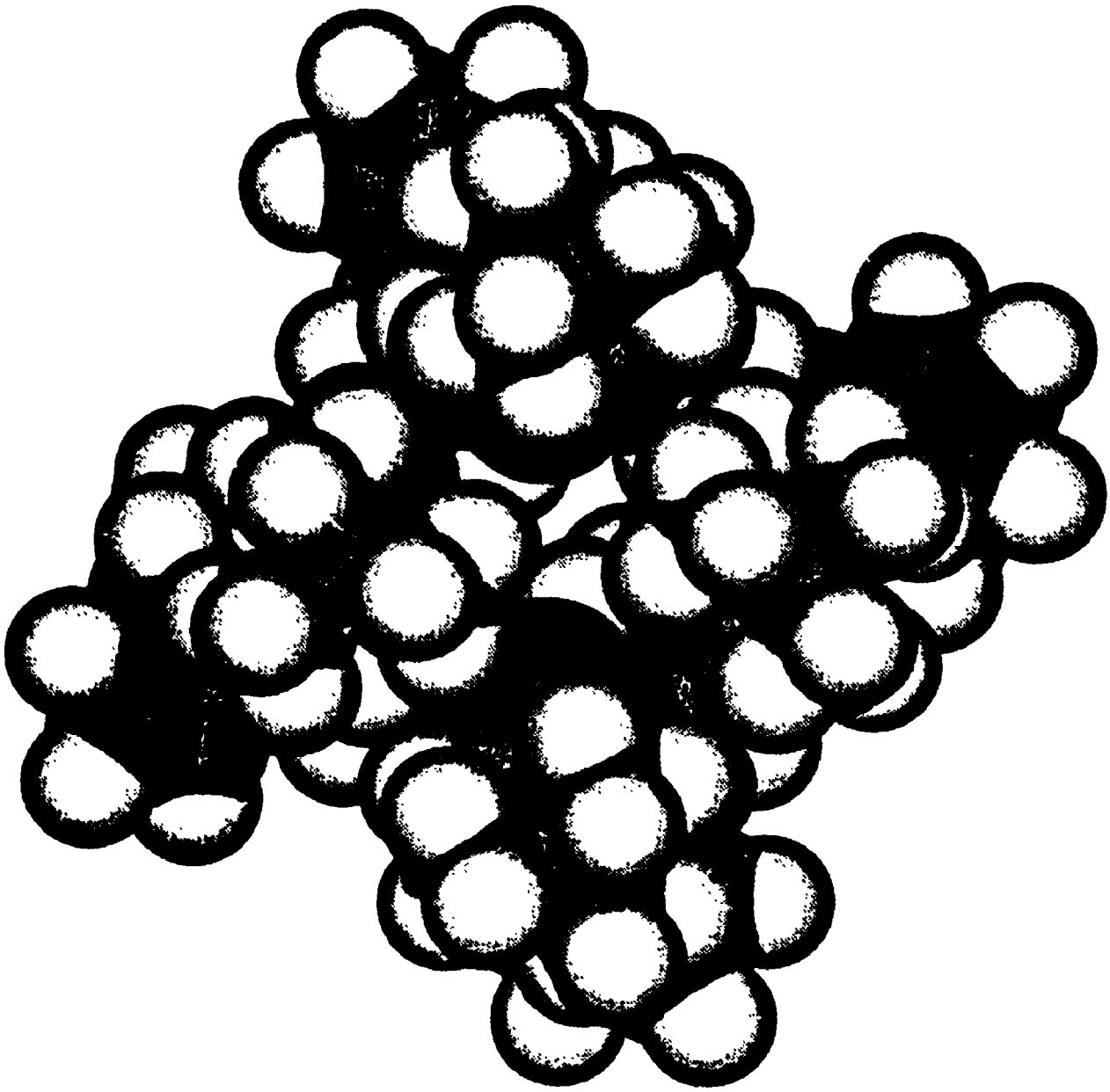
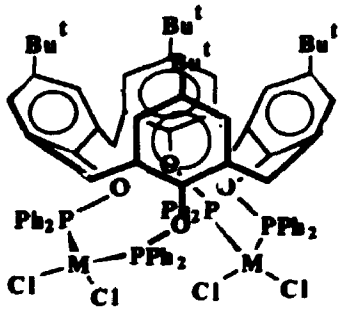


Figure 4. A space-filling model of the complex 4, showing the small cavity for guest inclusion

As expected, **2a** can either act as a monodentate ligand or as a chelating ligand. Reaction of $[PtCl_2(SMe_2)_2]$ or $[PdCl_2(PhCN)_2]$, with **2a** occurred with displacement of SMe_2 or PhCN to give the dimetal complexes, **5** (**5a**, M = Pt; **5b**, M = Pd) in which each metal is chelated by two phosphorus atoms. Though the four phosphorus atoms are still identical, as indicated by their ^{31}P NMR spectra, there are two different pairs of methylene ($ArCH_2Ar$) resonances in the ^1H NMR spectrum, indicating that the molecules no longer have four-fold symmetry (see Figure 3c). One of these pairs of resonances appears as two doublets at δ = 2.9 and 4.45, while the second pair appears as a doublet at δ = 2.9 and a doublet of triplets at δ = 5.9. The resonance with the extra triplet coupling is assigned to the protons on the CH_2 groups located between the chelating phosphorus atoms, and particularly to the two protons which are directed towards the metal atoms. These protons, embraced by the P-Pt-P ten-membered ring, couple not only to the geminal hydrogen but also to the two adjacent phosphorus atoms through space. This unusual ^1H-^{31}P through space coupling was confirmed by excluding all other proton couplings by the homonuclear decoupling technique and by recording the COSY spectrum (see Figure 5). Molecular mechanics calculations[25] also indicate that the distance between H_a and the near ^{31}P atom is only 2.79 Å, and so it is reasonable to expect this through space coupling.



5 (5a: M=Pt; 5b: M=Pd)

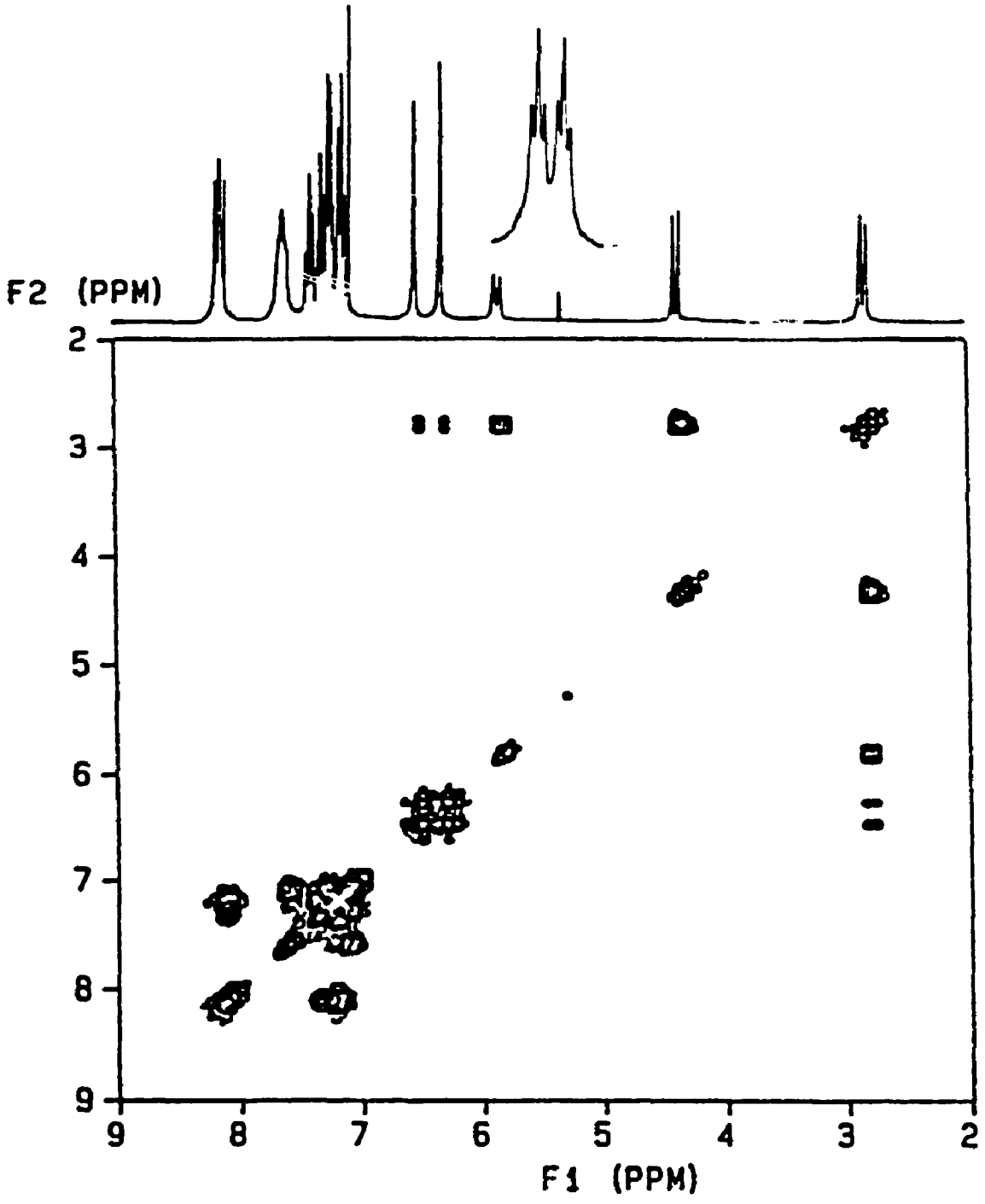


Figure 5. The two-dimensional ^{1}H-^{1}H correlated NMR spectrum (COSY) of complex **5a**. The triplet coupling in the resonance at $\delta = 5.9$ is shown in the expansion. Note that two resonances overlap accidentally at $\delta = 2.9$ and the correlations with resonances at $\delta = 5.9$ and 4.45 are clear.

6.3 CONCLUSIONS

When phosphinite groups are introduced into the lower rim of the calix[4]arene, the trisubstituted derivatives are more stable to hydrolysis than the tetrasubstituted derivatives. This is proposed to be due to lower steric strain in the trisubstituted compound. The introduction of bulky substituents, such as the Ph_2P groups described here, on the lower rim of the calixarene is also expected to affect the geometry of the bowl such that the bulky Bu^t groups on the upper rim will be forced closer together and so reduce the size of the entrance to the bowl. The introduction of additional metal substituents accentuates this effect. Thus, for example, the complexes **5** are easily hydrolysed back to **1a**, presumably due to steric strain. If the bowl opens sufficiently to allow access of a small guest molecule, the substituents on the lower rim will be pushed together and the resultant steric strain may accelerate the hydrolysis reactions.

6.4 EXPERIMENTAL SECTION

$[AuCl(SMe_2)]$,[13] $[PtCl_2(SMe_2)_2]$,[14] $[PdCl_2(PhCN)_2]$,[15] and *p-tert*-butyl-calix[4]arene[16] were prepared by literature methods. NMR spectra were recorded by using a Varian Gemini 300MHz spectrometer. ^1H chemical shifts were measured relative to partially deuterated solvent peaks, but are reported relative to tetramethylsilane. ^{31}P NMR chemical shifts were determined relative to 85% H_3PO_4 as an external standard. IR spectra were recorded on a Bruker IFS32 FTIR spectrometer with Nujol mulls. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN, USA.

6.4.1 *p-tert*-Butyl-calix[4]arene(OPPh$_2$)$_4$

2a, was prepared as described in the literature.[9,11] The ^{1}H NMR spectrum is in good agreement with the literature.[11] The ^{31}P NMR spectrum gives a singlet at δ = 123 (Lit. δ = 29.27, note the large discrepancy[11]) in CD_2Cl_2.

6.4.2 *p-tert*-Butyl-calix[4]arene(OPPh$_2$)$_3$(OH) 2c

Bu^{n}Li (2.5M, 2mL) was added at room temperature to a THF (15mL) suspension of *p-tert*-butyl-calix[4]arene **1** (1g, 1.54mmol). An orange solution was formed. Then the mixture was cooled to 0°C and ClPPh$_2$ (1.14ml, 6.25mmol) was added slowly. The mixture was kept at 0°C for 2 h. and then warmed to room temperature and stirred for 12h. The resulting brown solution was heated to 60°C and kept at this temperature for another 48 h. Most of the solvent was then evaporated under vacuum. MeCN (2?mL) was added and the mixture was cooled to 0°C for 4h, when **2c** (1.15g, 62.1%) was precipitated as a white solid, which was washed with MeCN and dried under vacuum. Anal. Calc for **2c** $C_{80}H_{83}O_4P_3$.MeCN: C, 79.3; H, 7.0; Found: C, 79.1; H, 6.8%. Spectroscopic data of **2c**: NMR in CD_2Cl_2: $\delta(^{31}P)$ = 121.8[s, 2P] and 112.9[s, 1P]. $\delta(^1H)$ = 1.11[s, 18H, t-Bu], 1.21[s, 9H, t-Bu], 1.15[s, 9H, t-Bu], 2.78[d, $^2J_{HH}$ = 13.2Hz, 2H, C$\underline{H}_2$], 3.78[d, $^2J_{HH}$ = 15.6Hz, 2H, C$\underline{H}_2$], 4.25[d, $^2J_{HH}$ = 14.9Hz, 2H, C$\underline{H}_2$], 4.20[d, $^2J_{HH}$ = 13.4Hz, 2H, C$\underline{H}_2$], 6.6-7.84, [PC$_6\underline{H}_5$, and CC$_6\underline{H}_5$], 1.97[s, 3H, C$\underline{H}_3$CN]. IR: ν_{OH}=3351cm^{-1}.

6.4.3 *p-tert*-Butyl-calix[4]arene(OPPh$_2$.AuCl)$_3$(OH) 3

A mixture of [AuCl(SMe_2)] (0.147g, 0.50mmol) and *p-tert*-butyl-calix[4]arene($OPPh_2$)$_3$(OH), **2c**, (0.20g, 0.167mmol) in CH_2Cl_2 was stirred at room temperature for 15 h. The CH_2Cl_2 and SMe_2 were removed completely under vacuum The residue was redissolved in CH_2Cl_2 (4mL) and crystallized by diffusion with MeCN (10mL). A white solid (0.17g, yield 53.6%) was obtained, washed with MeCN and dried under vacuum. Anal. Calc for **3** $C_{80}H_{83}Au_3Cl_3O_4P_3.CH_2Cl_2$: C, 49.1; H, 4.3; Found: C, 48.7; H, 4.0%. Spectroscopic data of **3**: NMR in CD_2Cl_2: $\delta(^{31}P)$ = 117.8 [s, 2P], 114.8 [s, 1P]. $\delta(^1H)$ = 0.93 [s, 18H, t-Bu], 0.99 [s, 9H, t-Bu], 1.25 [s, 9H, t-Bu], 2.91 [d, $^2J_{HH}$ = 12Hz, 2H, C$\underline{H}_2$], 3.16 [d, $^2J_{HH}$ = 14.8Hz, 2H], 3.38 [d, $^2J_{HH}$ = 14.8 Hz, 2H], 3.51 [s, 1H, O$\underline{H}$], 3.66 [d, $^2J_{HH}$ = 13.6Hz, 2H, C$\underline{H}_2$], 6.59 [t, J_{HH}=4.6Hz, 4H, ArH], 6.95 [d, J_{HH}=8.4H, 4H, ArH], 7.3-7.9 [m, 30H, $PC_6\underline{H}_5$], 5.33 [s, 2H, CH_2Cl_2]. IR: ν_{OH}=3366cm^{-1}.

6.4.4 *p-tert*-Butyl-calix[4]arene($OPPh_2AuCl$)$_4$, 4a

A mixture of [AuCl(SMe_2)] (0.17g, 0.58mmol) and *p-tert*-butyl-calix[4]arene($OPPh_2$)$_4$, **2a**, (0.20g, 0.145mmol) in CH_2Cl_2 (20mL) was stirred at room temperature for 15 h. The CH_2Cl_2 and SMe_2 were removed completely under vacuum. The residue was redissolved in CH_2Cl_2 and crystallized by diffusion with MeCN. Platelike colourless crystals (0.25g, yield 74.5%) were obtained, washed with MeCN and dried under vacuum. Spectroscopic data of **4a**: Anal. Calc for **4a** $C_{92}H_{92}Au_4Cl_4O_4P_4.MeCN$: C, 47.9; H, 4.1; Found: C, 48.1; H, 4.2%. NMR in CD_2Cl_2: $\delta(^{31}P)$ = 115.9 [s]. $\delta(^1H)$ = 1.03 [s, 36H, t-Bu], 1.97 [s, 3H, C$\underline{H}_3$CN], 2.61 [d, $^2J_{HH}$ = 13.2Hz, 4H, C$\underline{H}_2$], 4.44 [d, $^2J_{HH}$ = 13.2Hz, 4H, C$\underline{H}_2$], 6.69 [s, 8H, Ar$\underline{H}$)], 7.15-7.20 [m, 16H, $PC_6\underline{H}_5$, meta to P], 7.42-7.48 [m, 8H, $PC_6\underline{H}_5$, para to P], 7.62-

7.70 [m, 16H, $PC_6\underline{H}_5$, ortho to P].

6.4.5 *p-tert*-Butyl-calix[4]arene($OPPh_2AuCCPh$)$_4$ 4b

A mixture of [$(AuCCPh)_n$] (0.17g, 0.58mmol) and *p-tert*-butyl-calix[4]arene($OPPh_2$)$_4$ 2a (0.20g, 0.145mmol) in CH_2Cl_2 (20mL) was stirred at room temperature for 15 h. The same procedure as above was used and a white solid (0.19g, yield 49.9%) was obtained and washed with MeCN and dried under vacuum. Spectroscopic data of 4b: Anal. Calc for 4b $C_{124}H_{112}Au_4O_4P_4.CH_2Cl_2.MeCN$: C, 56.4; H, 4.4, Found: C, 56.5; H, 4.2%. NMR in CD_2Cl_2: $\delta(^{31}P)$ = 132.3 [s]. $\delta(^1H)$ = 1.04 [s, 36H, t-Bu], 1.97 [s, 3H, $C\underline{H}_3CN$], 2.69 [d, $^2J_{HH}$ = 13.4Hz, 4H, $C\underline{H}_2$], 4.57 [d, $^2J_{HH}$ = 13.4Hz, 4H, $C\underline{H}_2$], 5.30 [s, 4H, $C\underline{H}_2Cl_2$], 6.70 [s, 8H, Ar$\underline{H}$], 7.07-7.84 [m, 68H, $PC_6\underline{H}_5$, and $CC_6\underline{H}_5$].

6.4.6 *p-tert*-Butyl-calix[4]arene($OPPh_2$)$_4$($PtCl_2$)$_2$ 5a

A mixture of [$PtCl_2(SMe_2)_2$] (0.12g, 0.30mmol) and *p-tert*-butyl-calix[4]arene($OPPh_2$)$_4$, 2a, (0.20g, 0.145mmol) in CH_2Cl_2 (20mL) was stirred at room temperature for 15 h. The CH_2Cl_2 and SMe_2 were removed completely under vacuum. The residue was redissolved in CH_2Cl_2 and crystallized by diffusion with MeCN. A white solid (0.18g, yield 67.1%) was obtained, washed with MeCN and dried under vacuum. Anal. Calc. for 5a $C_{92}H_{92}Cl_4P_4Pt_2O_4.MeCN$: C, 57.6; H, 4.9. Found: C, 57.9; H, 5.1%. Spectroscopic data of 5a: NMR in CD_2Cl_2: $\delta(^{31}P)$ = 83.5 [s, $^1J_{Pt-P}$ = 4364.5Hz]. $\delta(^1H)$ = 0.90 [s, 36H, t-Bu], 2.01 [s, 3H, $C\underline{H}_3CN$], 2.88 [d, 2H, $^2J_{HH}$ = 14Hz, $C\underline{H}_2$, exo], 2.91 [d, 2H, $^2J_{HH}$ = 14Hz,

$C\underline{H}_2$, exo to P-Pt-P ten-membered ring], 4.49 [d, 2H, $^2J_{HH}$ = 14Hz, $C\underline{H}_2$, endo], 5.85 [dt, 2H, $^2J_{HH}$ = 14Hz, $^5J_{PH}$ = 3.4Hz, $C\underline{H}_2$, endo to P-Pt-P ten-membered ring], 6.30 [s, 4H, Ar$\underline{H}$, endo to P-Pt-P ten-membered ring], 6.47 [s, 4H, Ar$\underline{H}$, exo to P-Pt-P ten-membered ring], 7.33-7.46 [m, 16H, $PC_6\underline{H}_5$, para to P], 7.60-7.70 [m, 8H, $PC_6\underline{H}_5$, meta to P], 8.12-8.22 [m, 16H, $PC_6\underline{H}_5$, ortho to P].

6.4.7 *p-tert*-Butyl-calix[4]arene$(OPPh_2)_4(PdCl_2)_2$ 5b

A mixture of $[PdCl_2(PhCN)_2]$ (0.08g, 0.29mmol) and *p-tert*-butyl-calix[4]arene$(OPPh_2)_4$ 2a (0.20g, 145mmol) in CH_2Cl_2 (20mL) was stirred at room temperature for 15 h. The CH_2Cl_2 and SMe_2 were removed completely under vacuum. The residue was redissolved in CH_2Cl_2 and crystallized by diffusion with MeCN A white solid (0.11g, yield 43.7%) was obtained, washed with MeCN and dried under vacuum. Anal. Calc for 5b $C_{92}H_{92}Cl_4P_4Pd_2O_4$.MeCN: C, 63.4; H, 5.4. Found: C, 63.8; H, 5.4%. Spectroscopic data of 5b: NMR in $CDCl_3$: $\delta(^{31}P)$ = 115.7[s]. $\delta(^1H)$ = 0.89 [s, 36H, t-Bu], 2.07 [s, 3H, $C\underline{H}_3CN$], 2.78 [d, 2H, $^2J_{HH}$ = 13.6Hz, $C\underline{H}_2$, exo], 2.81 [d, 2H, $^2J_{HH}$ = 13.6Hz, $C\underline{H}_2$, exo to P-Pt-P ten-membered ring], 4.38 [d, 2H, $^2J_{HH}$ = 14Hz, $C\underline{H}_2$, endo], 5.90 [dt, 2H, $^2J_{HH}$ = 14Hz, $^5J_{PH}$ = 3.4Hz, $C\underline{H}_2$, endo to P-Pt-P ten-membered ring], 6.28 [s, 4H, Ar$\underline{H}$, endo to P-Pt-P ten-membered ring], 6.48 [s, 4H, Ar$\underline{H}$, exo to P-Pt-P ten-membered ring], 7.33-7.47 [m, 16H, $PC_6\underline{H}_5$, para to P], 7.55-7.70 [m, 8H, $PC_6\underline{H}_5$, meta to P], 8.10-8.24 [m, 16H, $PC_6\underline{H}_5$, ortho to P].

6.4.8 Crystal Structure Data of 1a.MeCN

$C_{44}H_{56}O_4.CH_3CN$, M = 689.98, T = 123 K, tetragonal, space group P4/n (origin at $\bar{1}$, a = 12.7194(4), c= 12.7668(3) Å, V = 2065.5(11) Å^3, Z = 2, D_{calc} = 1.109 g cm^{-3}, F(000) = 748, Mo-Kα X-rays, λ = 0.71073 Å, μ = 0.65 cm^{-1}.

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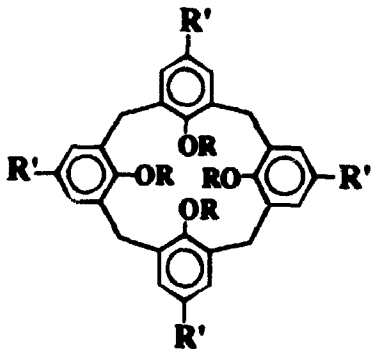
Chapter Seven

SILVER ION INCLUSION BY CALIX[4]ARENE ETHERS

7.1 INTRODUCTION

Calix[4]arenes are cyclic molecules which contain four phenyl rings linked by methylene bridges There has been much recent interest in their ability to act as hosts for cations since they display high affinity and high selectivity for cation inclusion.[1,2] Calix[4]arenes are useful building blocks for more complex molecules with unusual properties, but their ability to act as hosts is strongly influenced by their conformations. Four different orientations of the phenyl rings of the cyclic tetramer are possible as illustrated in Figure 1.[2,3] Most calix[4]arenes with OH groups, such as compounds **1** and **2**, exist preferentially in the cone conformation because of hydrogen bonding effects. However, O-alkyl calix[4]arenes such as the methyl ethers, **3** and **4**, shown in Figure 1 are conformationally flexible at room temperature. Control of the conformation of O-alkylated calix[4]arenes is highly desirable in terms of both their functionalization and their host-guest chemistry.



1. R = H, R' = H; **2**. R = H, R' = Bu^t
3. R = Me, R' = H; **4**. R=Me, R' = Bu^t

Calix[4]arenes are already known to form complexes with some transition metals.[4-9] In most of these cases, the transition metals have been firmly bound and the coordination is irreversible. The π-electron-rich calix[4]arene ethers, which possess two sets of face-to-face benzene rings, offer an interesting site for complexation. This chapter reports the reversible inclusion of transition metal cations and the effects of their complexation on the conformation and fluxionality of the calix[4]arene host. It will be shown that the reciprocal recognition between the calix[4]arene hosts and silver ion guest involves coordination of the silver cation to the electron-rich aryl groups of the calix[4]arene ethers.

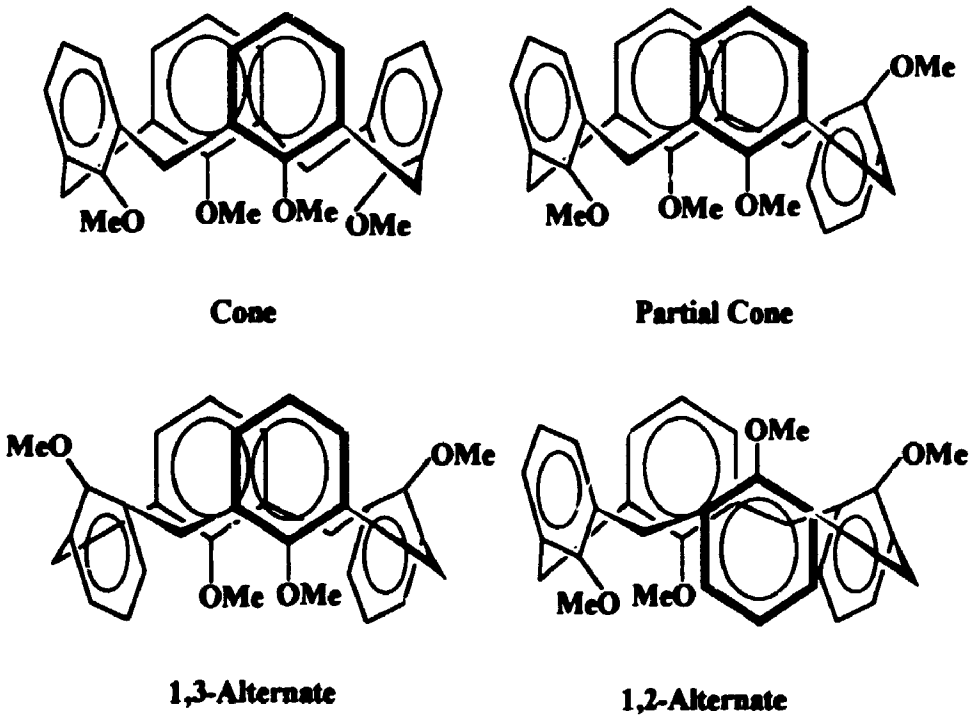


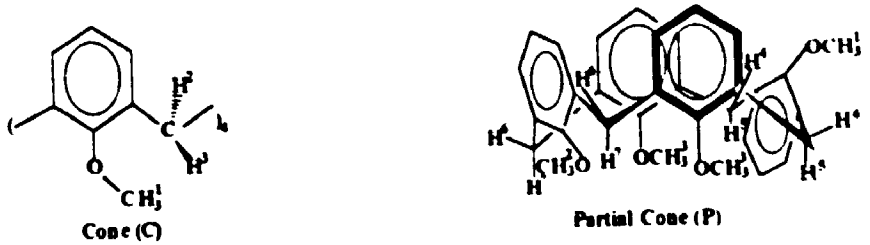
Figure 1. Conformations of calix[4]arene ethers

7.2 RESULTS AND DISCUSSION

7.2.1 Preparation of Calix[4]arene-Silver Complexes, 5

All previously reported silver complexes of simple arenes, such as the relatively stable complex $[Ag(PhCH_2CH_2Ph)]^+$, decompose rapidly unless they are stored in the presence of excess ligand vapor and protected from moisture.[10,11] The silver complexes of deltaphane, paracyclophane and stilbene, however, are crystalline solids, which are stabilized by forming two or three coordinate bonds in the complexes 7, 8 and 9.[12-14] These are called π-cryptands.[15] The present work shows that calix[4]arenes, which have four phenyl rings arranged around a central cavity, can form unusually stable silver(I) complexes which are further examples of π-cryptands. Thus, slow evaporation of a stoichiometric solution of 3 and silver nitrate in dry tetrahydrofuran gave colorless or pale amber crystals of the new complex 5a. This complex dissolved in CH_2Cl_2 (320 mg mL^{-1}) and $CHCl_3$, in contrast to silver nitrate which is insoluble. Addition of silver nitrate in excess of the 1:1 stoichiometry caused no further changes to the ^1H NMR spectrum of 5a. Crystals of the new complex 5a are stable to moist air. Complex 5a is photosensitive since exposure of a solution in THF or CH_2Cl_2 solution over one week led to a color change from colorless to amber. The calix[4]arene-silver complexes, 5b and 5c, were prepared in a similar way by reaction of 3a with silver trifluoroacetate or silver hexafluorophosphate. These calix[4]arene silver complexes are also stable except that the hexafluorophosphate is rapidly hydrolyzed to give the $PO_2F_2^-$ anion. The sharp ^1H NMR signals of 5 at room temperature indicate that the silver-arene bonds are well formed since

the binding between calix[4]arene 3 and silver is strong enough to stop the conformational tumbling of 3 (Figure 2).



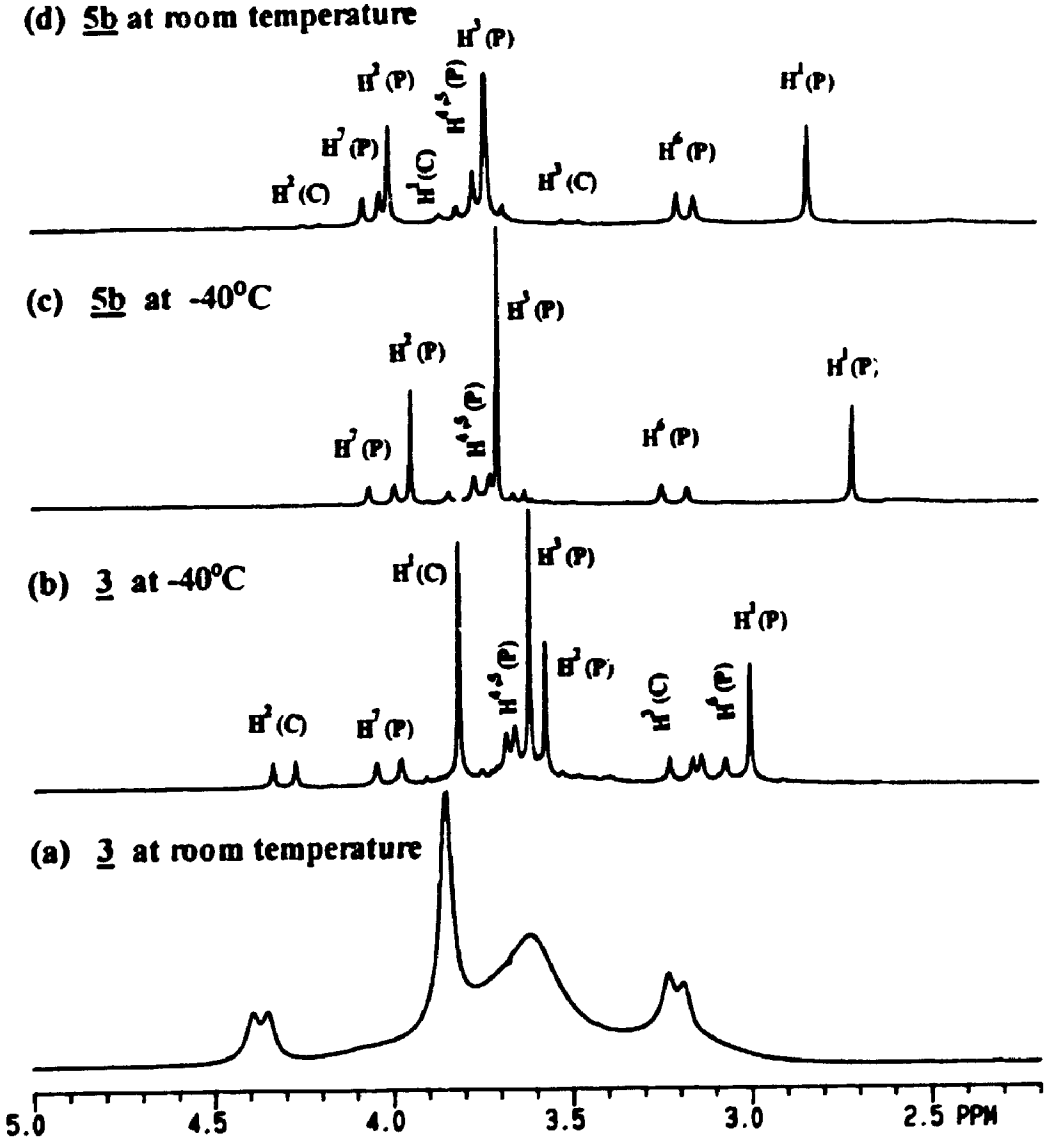
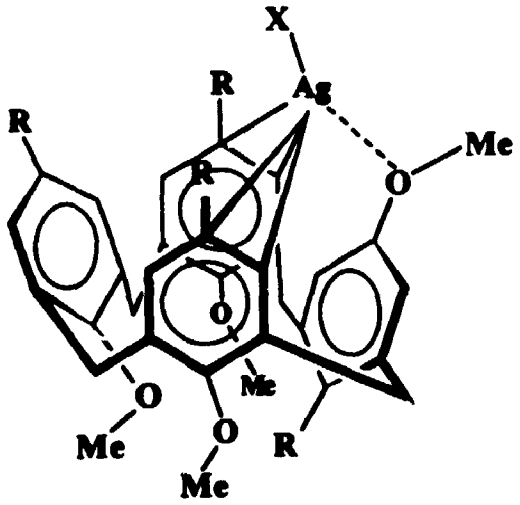
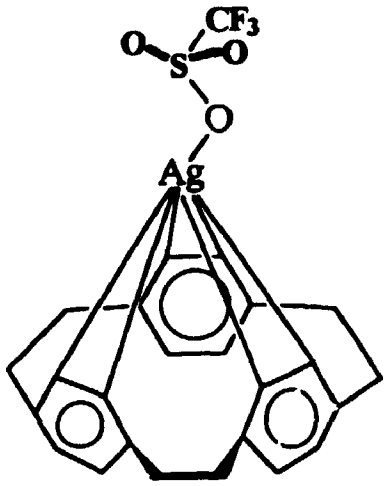


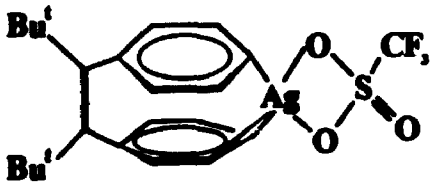
Figure 2. The ^1H NMR spectra of 3 and 5b in CD_2Cl_2
(The aryl parts are omitted for clarity. P: partial cone; C: Cone.)



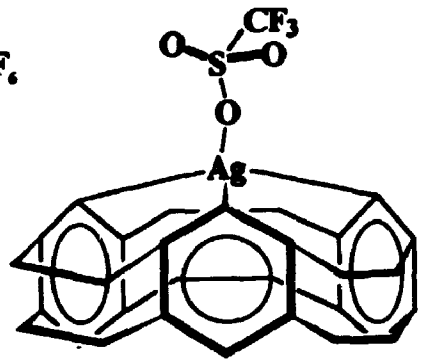
5a: R=H, X=$AgNO_3$; 5b: R=H, X=AgO_2CCF_3;
5c: R=H, X=$AgPF_6$; 6a R=Bu^t, X=$AgNO_3$;
6b: R=Bu^t, X=AgO_2CCF_3; 6c: R=Bu^t, X=$AgPF_6$



Paracyclophane 7



Cofacial Stilbene 9



Deltaphane 8

7.2.2 Molecular Structure of 5a

X-ray analysis shows that crystals of 5a obtained from THF/diethyl ether/n-hexane solution contain discrete molecules (Figure 3) in which the silver ion is bound both to the calix[4]arene and to an asymmetrically bidentate nitrate residue. The selected bond distances and bond angles are listed in Table 1. The molecule has an approximate plane of symmetry which contains the $AgNO_3$ unit and bisects phenyl rings 1 and 3 of the

calix[4]arene. In addition, the calix[4]arene adopts a partial cone conformation. The conformation is such that rings 2 and 4 are nearly co-facial (dihedral angle 12.7(2)°). The silver ion lies in the cleft between these rings: it is bound to them through the edges C(23)-C(24) and C(44)-C(45) and it is also attached to ring 3 through its MeO oxygen atom, O(31). The atoms of the calix[4]arene donor set [C(23), C(24), C(44), C(45) and O(31)] are coplanar to within 0.005(5) Å; the silver atom is displaced by 0.30 Å from this plane towards O(2), i.e. away from the interior of the calix[4]arene.

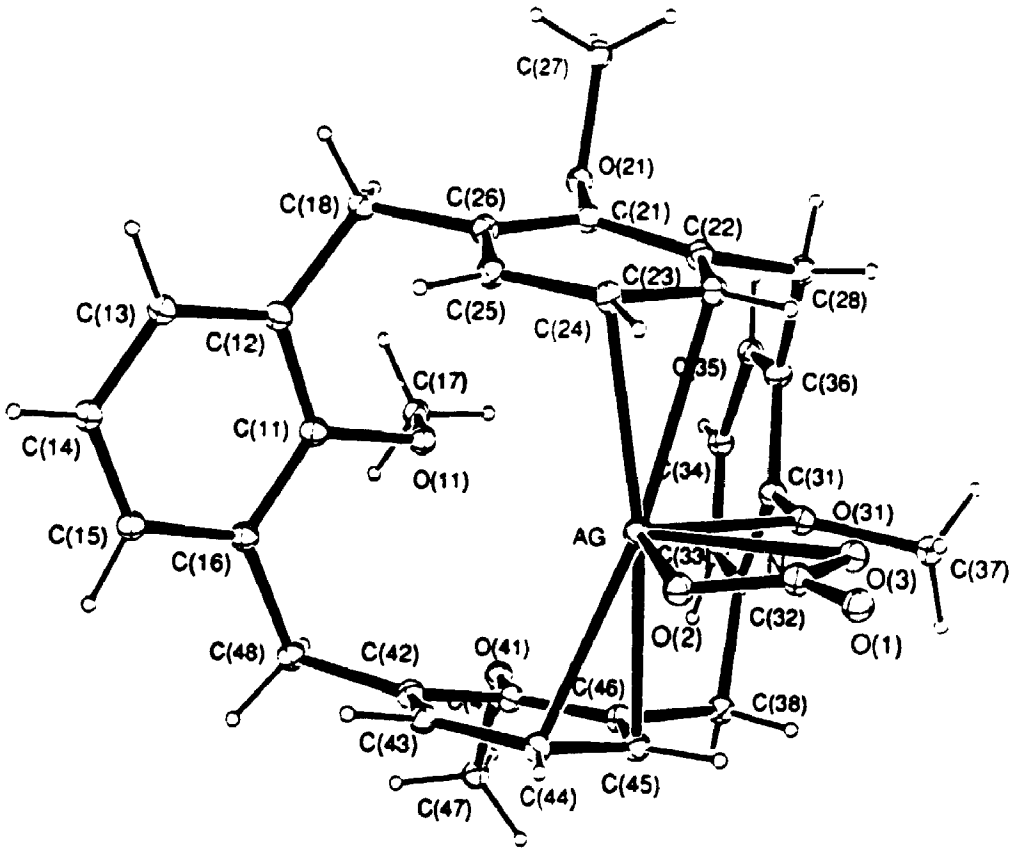


Figure 3. A view of the tetra-O-methylcalix[4]arene-silver nitrate complex, **5a**, showing the atom numbering scheme. atoms are represented as spheres of arbitrary radius.

Table 1. **Selected interatomic distances (Å) and angles (°) in 5a**

(a) Selected Bond Lengths (Å)

Ag-O(2)	2.389(6)	Ag-O(3)	2.705(8)	Ag-O(31)	2.517(3)
Ag-C(23)	2.643(5)	Ag-C(24)	2.504(5)	Ag-C(44)	2.527(5)
Ag-O(45)	2.549(5)	O(1)-N	1.174(6)	O(2)-N	1.209(7)
O(3)-N	1.157(7)				

	Range	Mean
C_{ar} - C_{ar}	1.351(9) - 1.410(6)	1.387(3)
C_{ar} - CH_2	1.501(7) - 1.530(7)	1.514(3)
O - C_{ar}	1.383(5) - 1.394(5)	1.389(3)
O - CH_3	1.418(6) - 1.451(6)	1.435(7)

(b) Selected Bond Angles (°)

O(2) - Ag - O(3)	44.0(2)	O(2) - Ag - O(31)	124.0(2)
O(2) - Ag - C(23)	103.5(3)	O(2) - Ag - C(24)	89.8(3)
O(2) - Ag - C(44)	88.1(3)	O(2) - Ag - C(45)	102.6(3)
O(3) - Ag - C(31)	80.7(2)	O(3) - Ag - C(23)	83.1(3)
O(3) - Ag - C(24)	92.0(3)	O(3) - Ag - C(44)	109.7(3)
O(3) - Ag - C(45)	101.1(3)	O(31) - Ag - C(23)	71.6(2)
O(31) - Ag - C(24)	102.5(2)	O(31) - Ag - C(44)	107.1(2)
O(31) - Ag - C(45)	75.7(2)	C(23) - Ag - C(24)	31.2(2)
C(23) - Ag - C(44)	166.9(2)	C(23) - Ag - C(45)	145.9(2)
C(24) - Ag - C(44)	145.5(2)	C(24) - Ag - C(45)	166.2(2)
C(44) - Ag - C(45)	31.6(2)	Ag - O(2) - N	110.9(4)
Ag - O(3) - N	95.3(5)	Ag - O(31) - C(31)	123.0(3)
Ag - O(31) - C(37)	123.1(3)	O(1) - N - O(2)	127.6(3)
O(1) - N - O(3)	122.4(6)	O(2) - N - O(3)	109.4(7)

The silver ion is thus attached to a rim of the calix[4]arene and does not completely occupy its central cavity as may be seen from Figure 4. Phenyl ring 1 and its associated methoxy group protect the silver ion from further ligation but do not interact with it covalently: the Ag...O(11) contact of 3.989(3) Å roughly *trans* to O(2) is clearly non-bonding. The silver coordination in **5a** resembles that found in deltaphane-silver complex **8**, in paracyclophane-silver complexes **7** and in cofacial stilbene **9**: in all these complexes

the silver atom is attached to one or more oxygen atoms of the counter-anion and lies on the rim of a cavity defined by electron-rich phenyl rings to which it is linked by between three and six π-Ag-C bonds. Thus, in **8** the Ag atom lies just outside the deltaphane cavity and is π-bonded to each phenyl ring through a single carbon atom;[14] in **9** the Ag-phenyl π-bonds involve ring edges rather tips;[13,14] in **9** both arrangements occur: one ring is bonded to silver through a single carbon atom, the other through a pair of adjacent carbon atoms.[12] The Ag-C distances of 2.50-2.64 Å in **5a** are fairly similar to those of 2.55-2.67 Å found in the perchlorate salt of paracyclophane-Ag^+;[13] a rather wider range of Ag-C bond lengths, 2.40-2.69 Å, was observed in deltaphane-Ag triflate.[14] In species such **8** and **9** the Ag coordination is completed by one or two strong Ag-O bonds of 2.36-2.51 Å. Similar in length to the shorter Ag-O bonds in **5a**. The partial cone conformation of the methoxy-calix[4]arene in **5a** thus provides a particularly favourable environment for formation of a π-cryptand complex since the silver can readily interact with a C_4O-calix[4]arene donor set. Ag^+ evidently prefers to lie on the rim rather than to occupy fully the cavity in such species. So far as we are aware, Cs^+ is the only metal cation whose presence in a calixarene cavity, stabilised by π-interaction with the calixarene phenyl rings, has been demonstrated by a diffraction study.[16]

Bond lengths and angles (Table 1) within the calix[4]arene residue are both internally consistent and in agreement with accepted values.[17] In particular, the C(23)-C(24) and C(44)-C(45) bond lengths [1.391(7) and 1.383(7) Å] do not differ significantly from the mean C_{ar}-C_{ar} bond length; nor are the C(31)-O(31) and O(31)-C(37) distances of 1.394(5) and 1.451(6) Å exceptional. Other authors, noting that arene ligands are little changed

geometrically by complexation to a silver ion, have concluded that the metal-ligand interaction in complex **5a** must be relatively weak.[12,13] The interaction of the silver cation with the nitrate group also appears normal: the Ag-O(2) and Ag-O(3) distances [2.39 and 2.71 Å] may be compared with the Ag-O bond lengths of 2.384(5)-2.702(8) Å in solid silver nitrate.[18]

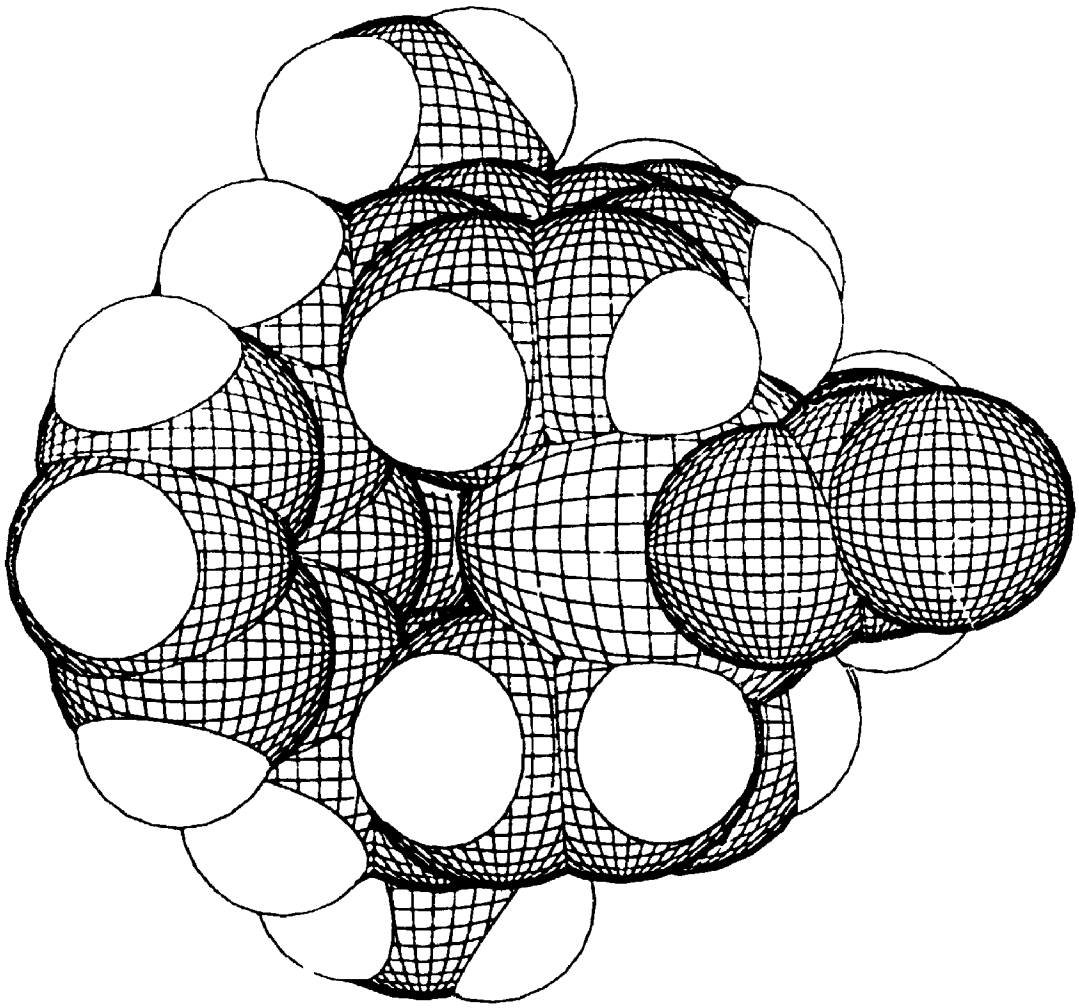


Figure 4. A view of a space-filling model of **5a**. The view direction is approximately the same as in Figure 3

7.2.3 Spectral Properties of the Calix[4]arene Silver Complexes, 5

It is known that the conformations of calix[4]arenes can be determined by the splitting pattern of the $ArCH_2Ar$ methylene protons in the ^1H NMR spectra and by the number of peaks in the ^{13}C NMR spectra, as shown schematically in Figure 5. Gutsche has shown that the tetramethyl ethers of 1 and 2 are conformationally flexible molecules. The ^1H NMR spectra of 3 and 4 recorded at room temperature at 100MHz showed broad signals that became sharp at lower temperature (-30°C). The spectra were interpreted in terms of two partial cone configurations, with a methoxy group pointed towards the center or outside of the cavity respectively.[3] However, from our 300 MHz ^1H NMR spectrum of 3 (Figure 2a and 2b), the molecule is fluxional at room temperature but , at -40°C, sharp spectra due to molecules in both cone and partial cone conformations are observed, with the ratio partial cone : cone = 4:1. In constrast, the ^1H NMR spectrum of **5b** (Figure 2c) at -40°C contains resonances due to the partial cone conformation only. There are major coordination shifts of the partial cone resonances as a result of the coordination to silver(I) as can be seen by comparing spectra **2b** and **2c** and the data in Table 2.

Table 2. Comparison of ^1H NMR chemical shifts of 3 and **5b** in partial cone conformation in CD_2Cl_2 at -40°C

	CH_3O-	Ar-CH_2-Ar
1(ppm)	2.99, 3.56, 3.61;	3.10(d), 4.00(d), 3.66(dd)
5(ppm)	2.70, 3.69, 3.94;	3.20(d), 4.02(d), 3.75(dd)
Δδ(Hz)	-87, 39, 99;	30, 6, 27,

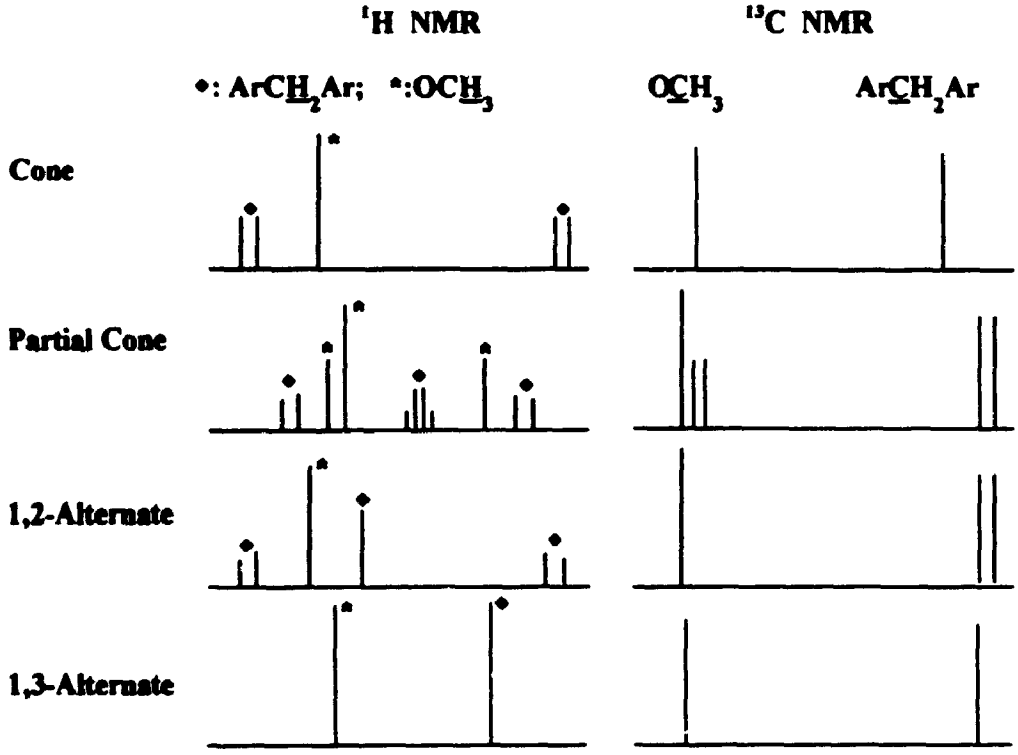


Figure 5. The ^{1}H NMR and ^{13}C NMR spectral patterns of the four possible conformers of calix[4]arene ethers

It is interesting to note that when silver(I) was added to the solution of **3**, the calix[4]arene-silver complexes **5** show sharp signals even at room temperature and the ratio of partial cone to cone conformers increased from 4:1 in **3** to 99.9:1 in **5b** (based on the integration of the ^{1}H NMR). Additional evidence for the existence of the two conformations and conformational distribution changes was obtained from the ^{13}C NMR spectra (Figure 6). The conformational abundances of these compounds are listed in Table 3. It is obvious that the P/C ratio is greatly increased upon silver ion complex formation.

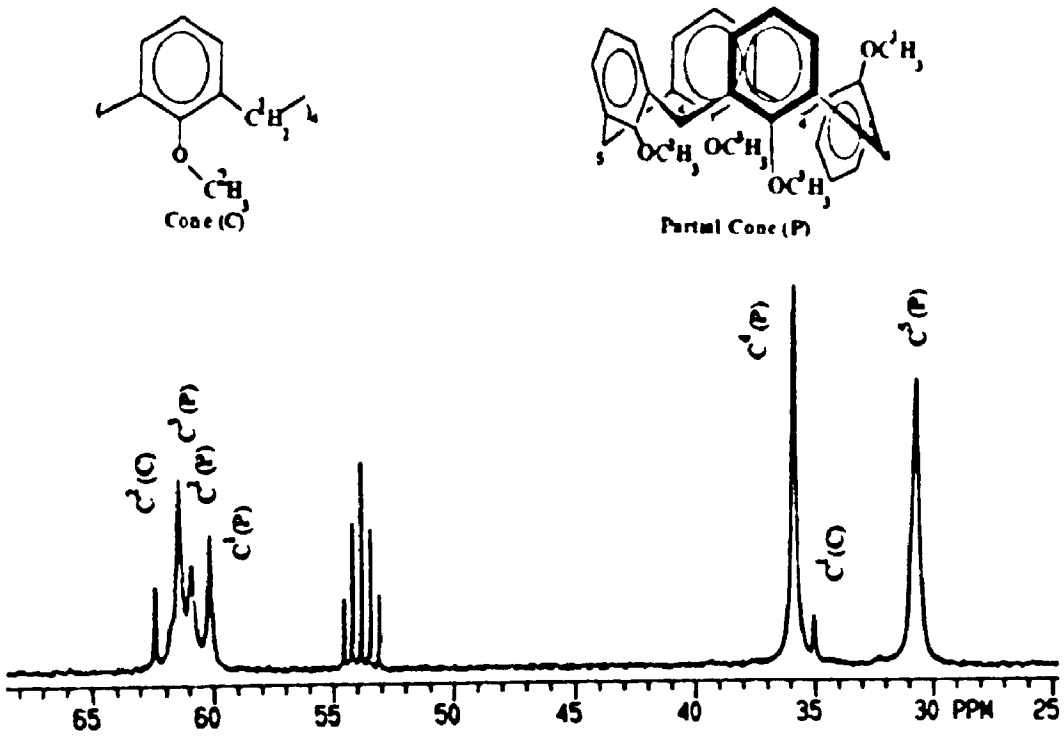


Figure 6. The ^{13}C NMR spectra of **5b** in CD_2Cl_2 at room temperature (The aryl parts are omitted for clarity. P: partial cone; C: Cone.)

Table 3. The conformation distribution of 3, 4, 5 and 6

	3	4	5a	5b	5c	6a	6b	6c
P/C r.t	--	--	99/1	99/1	95/5	--	--	98/1
P/C -40°C	80/20	92/8*	>99/1	>99/1	98/2	99/1	99/1	98/2

* Literature[3] reported value

** The data were obtained from integration of ^1H NMR spectra and ^{13}C NMR spectra.

The spectra were reproducible and so it is clear that the coordination of silver(I) to the calix[4]arene 3 has a marked effect on both the ratio of the conformers in solution and the rate of interconversion of the conformers. In particular, silver(I) stabilizes the partial cone conformation (although a small amount of calixarene-silver complex does exist in the cone conformation) and reduces the rate of interconversion of the conformers. It seems clear that the silver(I) ion must dissociate before the conformational equilibration can occur.

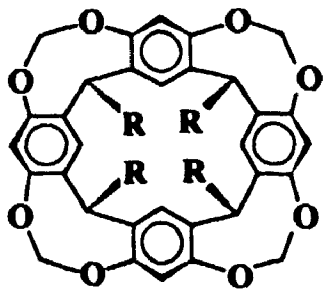
7.2.4 Thermal Properties of the Calix[4]arene-Silver Complexes, 5

The thermal properties of the new complexes 5a-5c have been studied by TGA and DSC. TGA of 5 shows that its decomposition temperature is lower than that of either of its precursors (see Figure 7). For example, compound 5b was half decomposed at ~280°C whereas ligand 3 and AgO_2CCF_3 decomposed at ~330 °C and 360 (m.p. of 3 234-235[3])°C respectively.

7.2.5 Factors Influencing the Complexing Ability of the Calix[4]arene Hosts

Both electronic effects and steric effects of substituents on the calix[4]arene derivatives on the formation of complexes 5 were investigated. Neither compound 1 nor 2 showed evidence for complex formation in the presence of silver trifluoroacetate as monitored by ^{1}H NMR. The complexation of silver salts with the cavitand 10, which has a rigid cone conformation has also been tested, but no evidence for complex formation with silver salts

was observed by ^{1}H NMR.



10, R = CH_2CH_2Ph

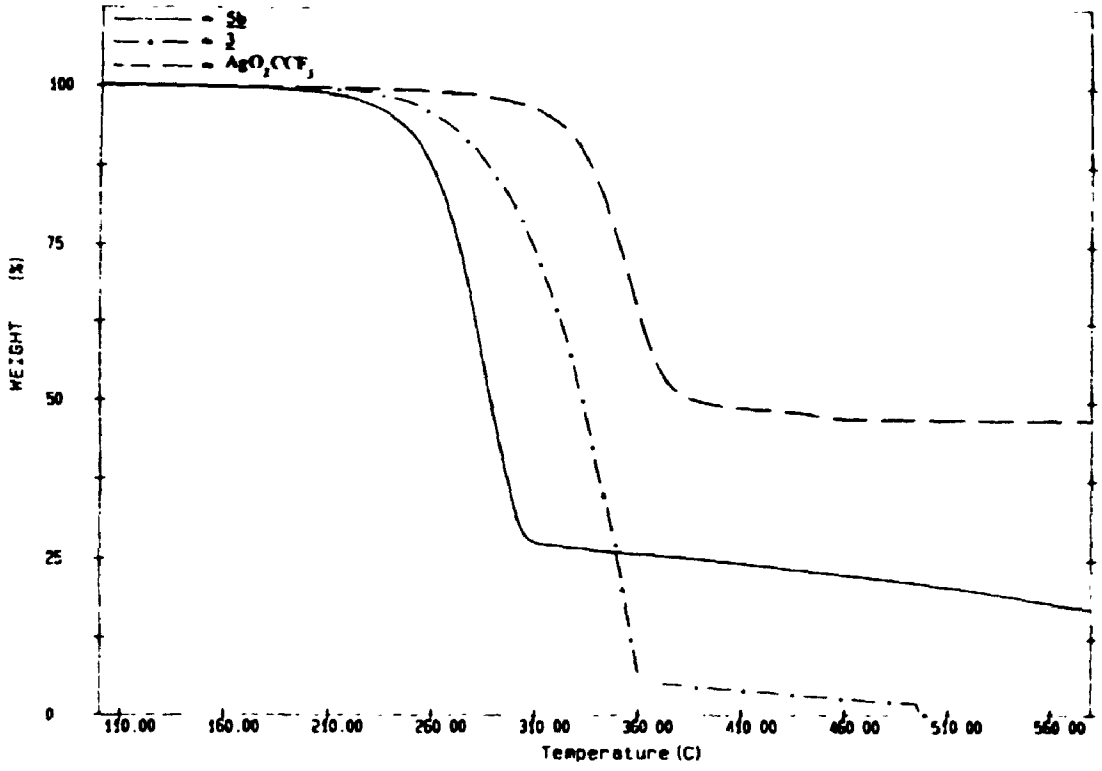


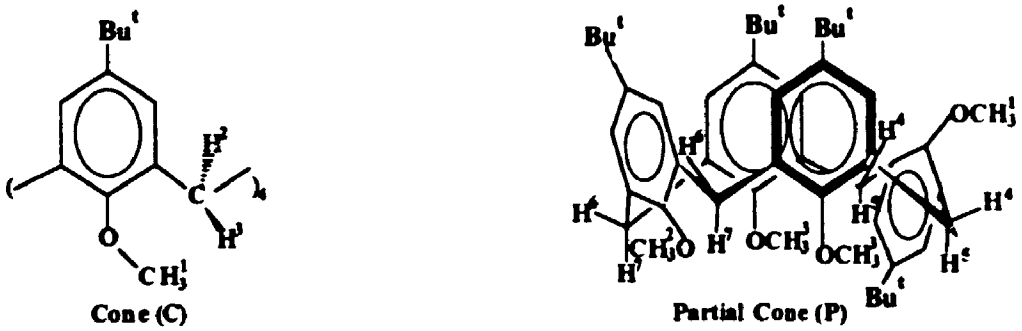
Figure 7. The TGA of **5b**, **3** and AgO_2CCF_3

In spite of the presence of bulky *t*-butyl substituents, compound **4** can interact with Ag(I)

($AgNO_3$, $AgOCOCF_3$ and $AgPF_6$). However, only complexation between **4** and $AgPF_6$ leads to relatively sharp peaks in the ^1H NMR spectrum at room temperature. The peaks in the ^1H NMR spectra of the other complexes, **6b** and **6c**, are broad but obvious chemical shift changes can be observed by comparison with the spectra of the precursors **4**. It is known that, at -25°C in $CDCl_3$, **4** consists of 2% cone, 92% partial cone, 5% 1,2-alternate and 1% 1,3-alternate conformers, as determined by ^1H NMR (400 MHz) measurements.[19] The interconversion of these conformers of **4** at room temperature is not completely stopped upon addition of silver ion. Only complexation between **4** and $AgPF_6$ gives sharp ^1H NMR resonances. Thus, there is probably a competition between coordination to silver(I) between the calixarene and the anion. Only with the most weakly coordinating anion $[PF_6]^-$, is the dissociation of Ag^+ from the silver-calix[4]arene complex sufficiently slow that the conformational tumbling of **4** appears slow on the NMR time scale. The relatively weak binding of silver(I) to this calixarene is attributed to steric hindrance due to the bulky t-butyl groups. If it is accepted that the calixarene fluxionality can only occur after dissociation of silver(I), the strength of the silver(I)-calixarene binding with respect to silver(I) anion binding will be important in determining the overall rate of interconversion of the calixarene conformers.

The ^1H NMR and ^{13}C NMR spectra of compounds **6** show that they prefer to stay in the partial cone conformation at low temperature (-40°C, Figure 8). Why is this so? Since coordination between the calix[4]arene and silver(I) will tend to draw two phenyl rings together and roughly parallel to each other, the resultant squeezing effect apparently decreases the relative thermodynamic stability of the cone conformation because of

increased steric crowding at the lower rim. The proposed structure for the silver(I)-calix[4]arene complex in the cone conformation is shown in Figure 9; it can be described as a "pinched cone" conformation.[20] Both the steric hindrance and a related electrostatic repulsion can be reduced by inversion of a phenyl unit to give the preferred partial cone conformation.



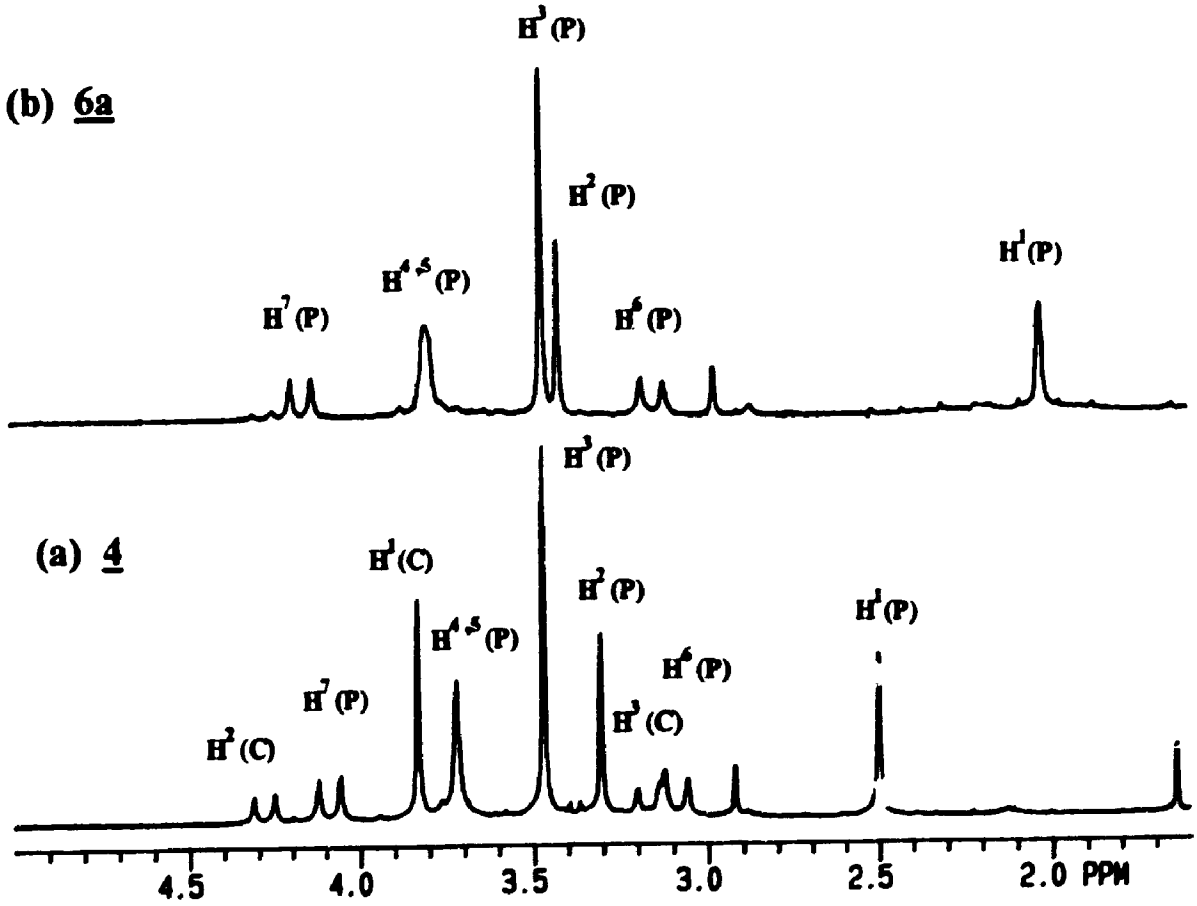


Figure 8. The ^{1}H NMR spectra of 4 and 6a in CD_2Cl_2 at -40°C
(The aryl parts are omitted for clarity. P: partial cone; C: Cone.)

Since only one set of resonances in the ^{1}H NMR and ^{13}C NMR spectra due to the cone conformation of 5 was observed, a fast equilibrium process in which the Ag^{+} ion moves rapidly between the opposite pairs of phenyl rings must occur to give apparent 4-fold symmetry (Figure 9).

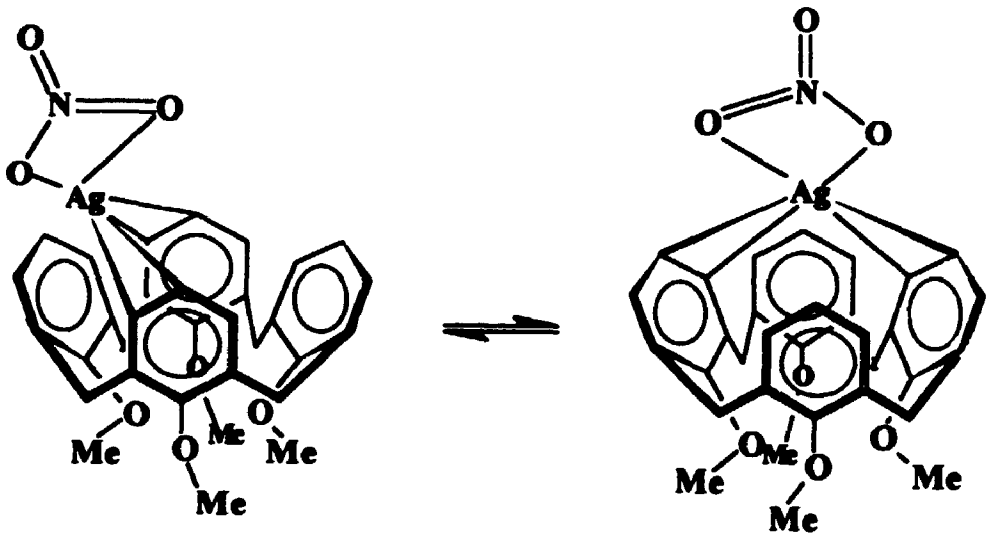


Figure 9. Molecular structure of calix[4]arene-silver complex in cone conformation

The inability of 1 or 2 to bind silver(I) may be due to the strong hydrogen bonding which locks the hosts into the cone conformation. Distortion to the "pinched cone" conformation, which is probably necessary to allow binding of silver(I), would lead to weakening of hydrogen bonding. The net result is that binding of silver(I) does not occur. As well as these subtle variations in the binding abilities of the hosts, it must be emphasized that the electrophilicity of silver(I) is strongly affected by its counterion, as summarized in Table 4. Based on the complexation with hosts 3 and 4, the affinities of

silver salts to ether calix[4]arenes fall in the series $AgPF_6$ > AgO_2CCF_3 > $AgNO_3$ > Ag_2SO_4, AgO_2CCH_3. Clearly, this series is the inverse of the coordinating ability of the anions.

Table 4. Reciprocal recognition between host, calix[4]arene or calix[4]resorcinarene ethers and guest, Ag(I) species.

Host	$AgPF_6$	AgO_2CCF_3	$AgNO_3$	Ag_2SO_4	AgO_2CCH_3
1	-	-	-	-	-
2	-	-	-	-	-
3	+	+	+	-	-
4	+	*	*	-	-
10	-	-	-	-	-

+:Obvious chemical shift changes can be observed by ^1H NMR.
-:No chemical shift changes can be observed by ^1H NMR.
*:Obvious chemical shift changes can be observed by ^1H NMR, but all the peaks are still broad and the ^1H NMR spectra at room temperature and at -40°C are different.

7.2.6 Competition Experiments

Competitive complexation experiments were performed by comparing the relative stability of 5 with other known silver arene complexes. Adding simple aromatic compounds, such as o-xylene, mesitylene or dibenzyl to the calix[4]arene-silver complexes, 5, did not cause changes in the ^1H NMR spectra in CD_2Cl_2 solution. However, when phenylacetylene or cyclohexene was added to the solution of 5, the silver ion is displaced and forms π-complexes with these more electron rich triple or double bonds with release of the free ligand, 3. When other weakly coordinating ligands such as MeCN or EtCN are present, the calix[4]arene-silver complexes cannot be formed. The silver ion can also be removed

from calix[4]arene-silver complexes by washing the solids **5** or **6** with MeCN.

7.3 CONCLUSIONS

The electron-rich calix[4]arene ethers in the partial cone conformation provide a suitable cavity to host the silver ion. The complexing ability of the calix[4]arene ether host for silver(I) is strongly influenced by both the steric and electronic effects of substituents on the calix[4]arene and the electrophilicity of the silver ion determines its ability to act as the guest. The binding of silver(I) is relatively weak and the silver can easily be removed by competition with stronger ligands. The silver calix[4]arene complexation provides a method to stop the conformational tumbling of the calix[4]arene and to lock it in the partial cone conformation.

7.4 EXPERIMENTAL SECTION

The calix[4]arenes, **1**,[3] 5,11,17,23-tetra-t-butyl-calix[4]arene, **2**,[21] 25,26,27,28-tetramethoxy-calix[4]arene, **3**,[3] 5,11,17,23-tetra-t-butyl-25,26,27,28-tetramethoxy-calix[4]arene, **4**,[3] 1,21,23,25-tetrakis(2-phenylethyl)-2,20:3,19-dimetheno-1H,21H,23H,25H-bis[1,3]dioxocino[5,4-i:5',4'-i']benzo[1,2-d:5,4-d']bis[1,3]benzodioxocin **7**,[22] were prepared by literature methods. M.P.s of all compounds were taken in unsealed capillary tubes using an electrothermal melting point apparatus. NMR spectra were collected by using a Varian XL300 spectrometer. ^{1}H and ^{13}C NMR chemical shifts were measured relative to partially deuterated solvent peaks, but are reported relative to

tetramethylsilane. Since the abundances of the cone, 1,3-alternate and 1,2-alternate conformers were low, only the spectral data of the dominant partial cone conformer are listed. IR spectra were recorded by using a Bruker IFS32 FTIR spectrometer with KBr mulls. Elemental analyses were performed by Galbraith Laboratories, Knoxville. Mass spectra were recorded by using a FINNEGAN MAT 8230 mass spectrometer.

7.4.1 25,26,27,28-Tetramethoxy-calix[4]arene.$AgNO_3$, 5a

A suspension of $AgNO_3$ (0.17g, 1mmol) in a solution of compound 3 (0.48g, 1mmol) in THF (30mL) was stirred for 12 h. at room temperature. A clear colorless solution was obtained. The volume of solvent was reduced and the remaining solution was then allowed to evaporate slowly over a period of 1 week. Colorless crystals of 5a (0.5g, yield 77%) were obtained. Anal. Calc. for $C_{32}H_{32}AgNO_7$: C, 59.09; H, 4.96; Found: C, 58 79; H, 4.75%. NMR in $CDCl_3$: $\delta(^1H)$ = 2.86 [s, 3H, $OC\underline{H}_3$], 3.75 [s, 6H, $OC\underline{H}_3$], 3.92 [s, 3H, $OC\underline{H}_3$], 3.18 [d, $^1J_{H\text{-}H}$ = 13.5Hz, 2H, $C\underline{H}_2$], 4.07 [d, $^1J_{H\text{-}H}$=13.5Hz, 2H, $C\underline{H}_2$], 3.66 [dd, AB system, 4H, $^1J_{H\text{-}H}$ = 14.2Hz, $C\underline{H}_2$], 6.62-7.36 [m, 12H, Ar$\underline{H}$]. $\delta(^{13}C)$ = 30 30 [s, 2C, $\underline{C}H_2$], 35.47 [s, 2C, $\underline{C}H_2$], 59.85 [s, 1C, $\underline{C}H_3$], 61.02 [s, 1C, $\underline{C}H_3$], 61.27 [s, 2C, $\underline{C}H_3$], 113.1-160.8 [m, 24C, Arene]. IR: $\nu_{N\text{-}O}$ = 1290, 1208, 1173cm^{-1}. FAB-MS: m/e = 587; calc. for $C_{32}H_{32}AgO_4^+$ 587.

7.4.2 Single Crystal X-ray Analysis of 5a

Single crystals of complex 5a were obtained as described above. All X-ray measurements

were made by K. W. Muir and A.A. Torabi with graphite-monochromated Mo radiation on an Enraf-Nonius CAD4 diffractometer using a transparent block-shaped crystal which slowly darkened in colour during the course of the experiment. Experimental detail are summarised in Table 5.

Table 5 Crystallographic data for tetra-O-methylcalix[4]arene silver nitrate , **5a**

Empirical Formula	$C_{32}H_{32}O_4.AgNO_3$
Formula Weight	650.48
Space Group	$P2_1/c$
Cell Dimensions	a = 10.0693(7) Å b = 24.6923(10) Å c = 11.4950(4) Å β = 92.609(4)° V = 2855.1(3) Å^3
Molecules in Unit Cell	4
D_{calc}, g.cm^{-3}	1.513
Crystal Dimmensions, mm	0.53 x 0.45 x 0.45
Temperature, °C	27.5
Radiation	MoKα
Wavelength, Å	0.71073
m(MoKα), cm^{-1}	7.45
Data Collection Range, θ(deg.)	0 - 30.5
Absorption Factors (on F)	0.78 - 1.44
Unique Reflections with $I > 3\sigma(I)$	4563
Parameters Refined	370
Discrepancy Factor, R	0.052
Rω	0.064
Largest Shift/esd Ratio	0.08
Range of Values in Final Difference Synthesis, eÅ^3	1.1- 1.0

7.4.3 25,26,27,28-Tetramethoxy-calix[4]arene.$AgOCOCF_3$, 5b

This was prepared similarly from $AgOCOCF_3$ (0.22g, 1mmol), compound **3** (0.48g,

1mmol) in THF (30 mL) and was isolated as a colorless crystalline solid **5b** (0.55g, yield 79%). Anal. Calc. for $C_{34}H_{32}AgF_3O_6$: C, 58.22; H, 4.60. Found: C, 57.96; H, 4.41%. NMR in CD_2Cl_2: $\delta(^1H)$ = 2.70 [s, 3H, $OC\underline{H}_3$], 3.71 [s, 6H, $OC\underline{H}_3$], 3.95 [s, 3H, $OC\underline{H}_3$], 3.20 [d, $^1J_{H-H}$ = 14.6Hz, 2H, $C\underline{H}_2$], 4.11 [d, $^1J_{H-H}$ = 14.6Hz, 2H, $C\underline{H}_2$], 3.75 [dd, AB system, 4H, $^1J_{H-H}$ = 14.1Hz, $C\underline{H}_2$], 6.57-7.32 [m, 12H, Ar$\underline{H}$]. $\delta(^{13}C)$ = 30.63 [s, 2C, $\underline{C}H_2$], 35.81 [s, 2C, $\underline{C}H_2$], 60.15 [s, 1C, $\underline{C}H_3$], 60.90 [s, 1C, $\underline{C}H_3$], 61.44 [s, 2C, $\underline{C}H_3$], 113.8-159.42 [m, 24C, Arene], 157.70 [q, 1C, $\underline{C}F_3$], 159.84 [s, 1C, $CF_3\underline{C}O_2$]. IR: ν_{C-O} = 1630(br), 1290, 1203cm^{-1}

7.4.4 25,26,27,28-Tetramethoxy-calix[4]arene.$AgPO_2F_2$, 5c

This was prepared similarly from $AgPF_6$ (0.253g, 1mmol), compound **3** (0.48g, 1mmol) in THF (30mL). Yield 0.6g, 84% Anal. Calc. for $C_{32}H_{32}AgF_2O_6P$: C, 55.75; H, 4.68. Found: C, 55.83; H, 4.44%. NMR in CD_2Cl_2: $\delta(^1H)$ = 2.67 [s, 3H, $OC\underline{H}_3$], 3.81 [s, 6H, $OC\underline{H}_3$], 4.04 [s, 3H, $OC\underline{H}_3$], 3.34 [d, $^1J_{H-H}$=14.6Hz, 2H, $C\underline{H}_2$], 4.12 [d, $^1J_{H-H}$=14.6Hz, 2H, $C\underline{H}_2$], 3.86[dd, AB system, 4H, $^1J_{H-H}$=13.5Hz, $C\underline{H}_2$], 6.72-7.48 [m, 12H, Ar$\underline{H}$]. $\delta(^{13}C)$ = 30.67 [s, 2C, $\underline{C}H_2$], 35.45 [s, 2C, $\underline{C}H_2$], 60.47 [s, 1C, $\underline{C}H_3$], 60.90 [s, 1C, $\underline{C}H_3$], 61.93 [s, 2C, $\underline{C}H_3$], 109.31-160.93 [m, 24C, Arene $\underline{C}$, cannot be assigned unanimous). $\delta(^{31}P)$ = =17.1[t, $^1J_{PF}$ = 1047.5Hz].

Similarly were prepared **5,11,17,23-tetra-t-butyl-25,26,27,28-tetramethoxy-calix[4]arene.$AgNO_3$ 6a:** Yield 74%. Anal. Calc. for $C_{48}H_{64}AgNO_7$: C, 65.90; H, 7.37. Found: C, 65.61; H, 7.50%. NMR in CD_2Cl_2 at -40°C: $\delta(^1H)$ = 1.08[s, 9H, $C(C\underline{H}_3)_3$],

1.16[s, 18H, $C(C\underline{H}_3)_3$], 1.34[s, 9H, $C(C\underline{H}_3)_3$], 2.03 [s, 3H, $OC\underline{H}_3$], 3.47 [s, 6H, $OC\underline{H}_3$], 3.42 [s, 3H, $OC\underline{H}_3$], 3.15 [d, $^1J_{H\text{-}H}$=12.6Hz, 2H, $C\underline{H}_2$], 4.16 [d, $^1J_{H\text{-}H}$=12.6Hz, 2H, $C\underline{H}_2$], 3.80 [s, br, 4H, $C\underline{H}_2$], 6.79-7.25 [m, 12H, Ar$\underline{H}$]. **5,11,17,23-tetra-t-butyl-25,26,27,28-tetramethoxy-calix[4]arene.AgO_2CCF_3, 6b**: Yield 76%. Anal. Calc. for $C_{50}H_{64}AgF_3O_6$: C, 64.86; H, 6.97. Found: C, 64.96; H, 6.78%. NMR in CD_2Cl_2 at -40°C : $\delta(^1H)$ = 1.12 [s, 9H, $C(C\underline{H}_3)_3$], 1.20 [s, 18H, $C(C\underline{H}_3)_3$], 1.35 [s, 9H, $C(C\underline{H}_3)_3$], 2.19 [s, 3H, $OC\underline{H}_3$], 3.81 [s, 6H, $OC\underline{H}_3$], 4.11 [s, 3H, $OC\underline{H}_3$], 3.44 [d, $^1J_{H\text{-}H}$ = 12.7Hz, 2H, $C\underline{H}_2$], 4.15 [d, $^1J_{H\text{-}H}$ = 12.7Hz, 2H, $C\underline{H}_2$], 3.86 [s, br, 4H, $C\underline{H}_2$], 6.90-7.18 [m, 12H, Ar$\underline{H}$]. **5,11,17,23-tetra-t-butyl-25,26,27,28-tetramethoxy-calix[4]arene.$AgPF_6$ 6c:** Yield 77%. Anal. Calc. for $C_{48}H_{64}AgF_6O_4P$: C, 60.19; H, 6.73. Found: C, 59.93; H, 6.48%. NMR in CD_2Cl_2 at room temperature: $\delta(^1H)$ = 1.23 [s, 9H, $C(C\underline{H}_3)_3$], 1.30[s, 18H, $C(C\underline{H}_3)_3$], 1.36[s, 9H, $C(C\underline{H}_3)_3$], 2.10 [s, 3H, $OC\underline{H}_3$], 3.15 [s, 6H, $OC\underline{H}_3$], 3.89 [s, 3H, $OC\underline{H}_3$], 3.46 [d, $^1J_{H\text{-}H}$ = 12.6Hz, 2H, $C\underline{H}_2$], 4.15 [d, $^1J_{H\text{-}H}$ = 12.6Hz, 2H, $C\underline{H}_2$], 3.78 [s, br, 4H, $C\underline{H}_2$], 6.92-7.43 [m, 12H, Ar$\underline{H}$].

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15. The term pi-prismand has been used to describe complexes such as **8** in which a prism-shaped cavity is defined by the planes of pi-donor phenyl rings.[19] For species such as **5a** and **10** the shape of the cavity is not obviously prismatic and π-cryptand seem to us a more suitable generic name for such complexes.

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Chapter Eight

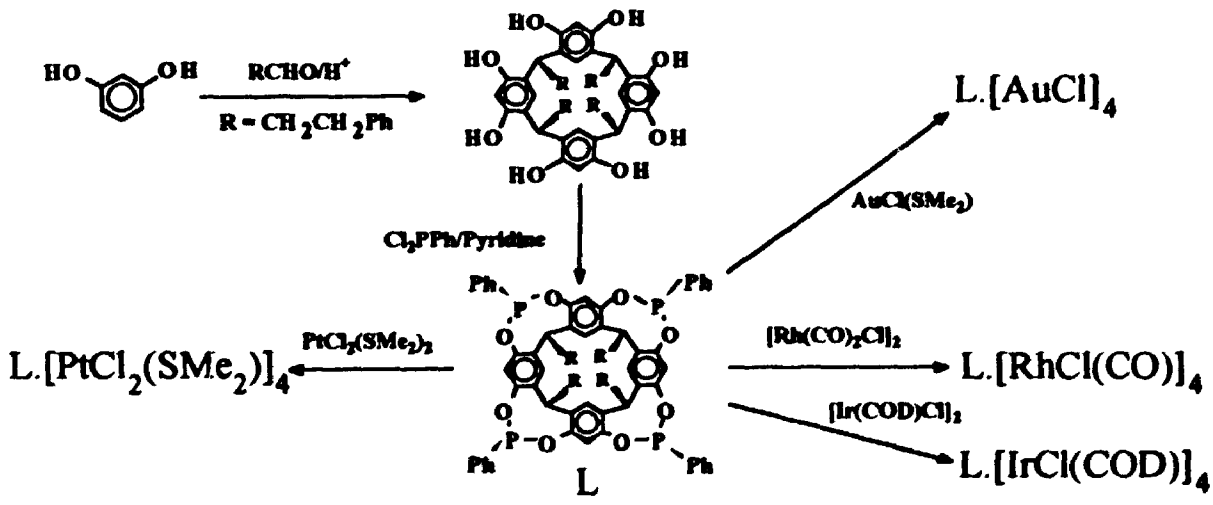
GENERAL CONCLUSIONS

The primary objective of the research was to establish an anion inclusion model system by introducing a set of transition metals on the rim of a macrocyclic ligand and to further investigate the supramolecular chemistry of the compounds prepared.

Our strategy was to functionalize the bowl shaped calixarenes and then to introduce transition metals on the rim of the calixarenes. During the course of the research, several significant achievements have been obtained, some of which are listed below.

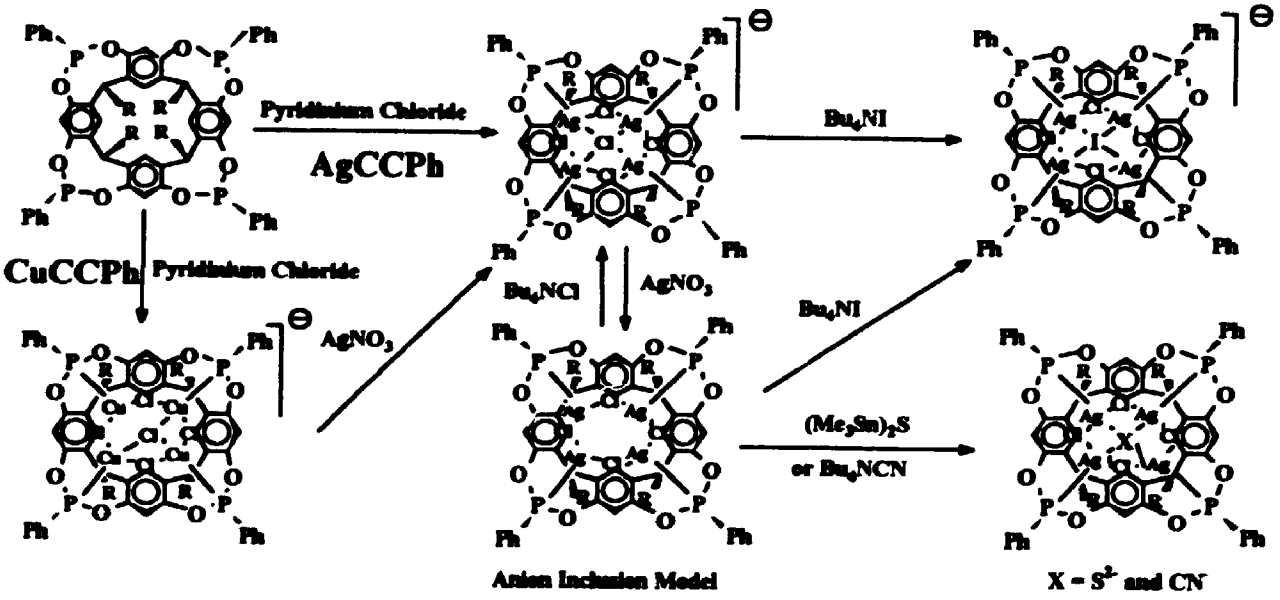
- Designed and synthesized a macrocyclic ligand, the phosphonite cavitand 1 which is able to coordinate with transition metals, such as Au(I), Pt(II), Rh(I) and Ir(I), to form transition metal rimmed cavitands as shown in Scheme I.

Scheme I



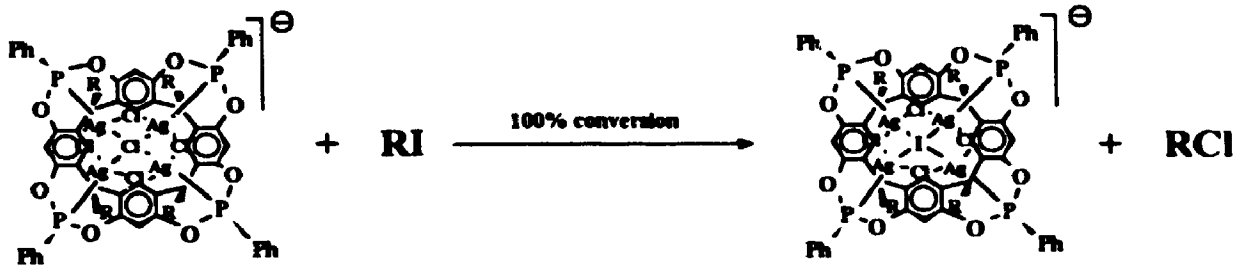
♦ Established a powerful anion receptor model system by introducing a set of electron-deficient transition metals on the upper rim of a calixresorcinarene as illustrated in Scheme II. Since anion inclusion is believed to be very important in many biological systems and enzyme reactions, this is a significant advance in the search for a model for anion inclusion. By modifying the anion receptor system, a more selective and more versatile anion receptor model system could be developed.

Scheme II



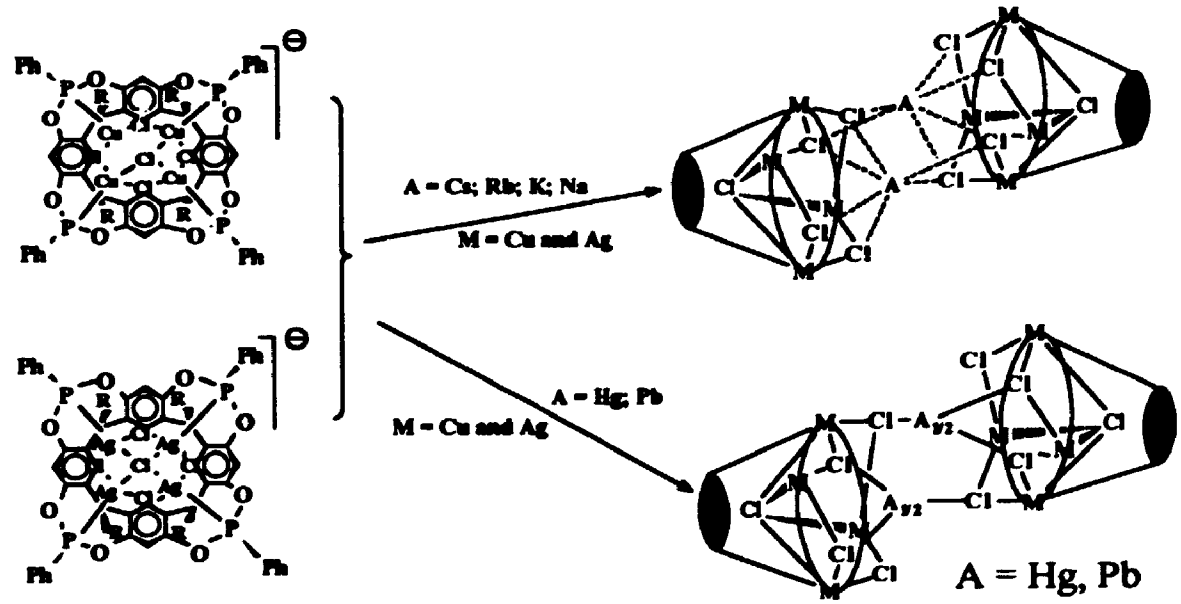
♦ Discovered that the nucleophilic properties of occluded anions are quite different from the free anions as illustrated in Scheme III. The selectivity of occluded anion in aliphatic nucleophilic substitution could be significant in organic synthesis.

Scheme III



◆ Investigated the metal cation coordination chemistry with the anionic bowl complexes as ligands and developed an unique cation receptor system as illustrated in Scheme IV. The novel anion inclusion system turned out to be a powerful and versatile metal cation receptor. This approach provided another unique cation receptor family.

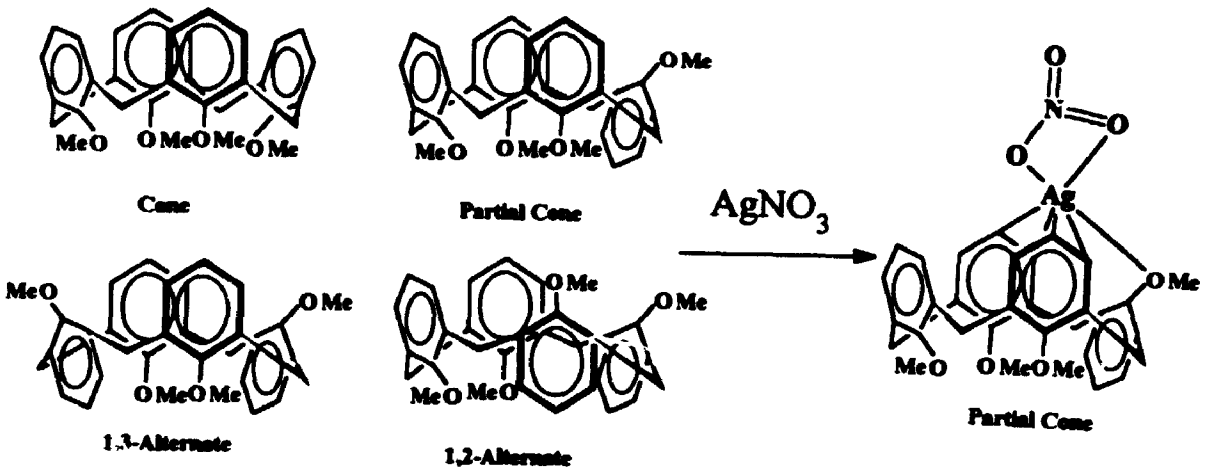
Scheme IV



◆ Discovered a "conformation freezer" to freeze out the conformational tumbling of calixarene ethers as illustrated in Scheme V. This discovery may have application in

functionalization of calixarenes and may provide structural information for an Ag^+ sensitive electrode.

Scheme V



In conclusion, the approach of introducing a set of transition metals on the macrocyclic ligands is a successful strategy in searching for a synthetic model for anion inclusion and it may also be a useful direction in searching for bio-mimetic catalysts.

APPENDIX I The crystal ionic radii (Å) of often used cations and anions

(a) Cation radii (Å)

Li^+	0.68;	Mg^{2+}	0.66;	Cr^{3+}	0.63;	Cu^{2+}	0.72;	Tl^+	1.50;
Na^+	0.97;	Ca^{2+}	0.99;	Mn^{2+}	0.80;	Ag^+	1.26;	Pb^{2+}	1.20,
K^+	1.33;	Sr^{2+}	1.16;	Fe^{2+}	0.74;	Zn^{2+}	0.74;		
NH_4^+	1.43;	Ba^{2+}	1.36;	Co^{2+}	0.72;	Cd^{2+}	0.97;		
Rb^+	1.49;			Ni^{2+}	0.69;	Hg^{2+}	1.11;		
Cs^+	1.67;								

(b) Anion radii(Å)

spherical:	F^-	1.33;	Cl^-	1.81;	Br^-	1.96;	I^-	2.20;	
linear:	OH^-	1.40;	CN^-	1.82;					
planar:	NO_2^-	1.55;	NO_3^-	1.89;	CO_3^{2-}	1.85;			
tetrahedral:	IO_3^-	1.82;	MnO_4^-	2.40;	SO_4^{2-}	2.30;	PO_4^{3-}	2.38.	

<<Quoted from *Handbook of CHEMISTRY and PHYSICS* and Shannon, R D and Prewitt, C. T. *Acta Crystallogr.*, **1969**, *B25*, 925>>